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High Temperature Dilute Acid Hydrolysis of Waste Cellulose: Batch and Continuous Processes

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HIGH TEMPERATURE DILUTE ACID HYDROLYSIS OF WASTE CELLULOSE: BATCH AND CONTINUOUS PROCESSES

by

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EPA-R-805239-030

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16. ABSTRACT

This 5-year investigation on the dilute acid hydrolysis of waste cellulose to glucose has emphasized the crucial step of continuously converting cellulose to glucose. Initial batch studies emphasized pretreatments to improve accessibility of the cellulose, and established suitable reaction conditions. Later a 1-ton/day pilot plant was designed and constructed based on the application of a Werner & Pfleiderer Twin Screw Extruder Reactor to demonstrate this approach. The process was tested using paper pulp (at 10% solids) and dry hardwood sawdust (at 95% solids). Attractive energy efficiencies and high conversion yields resulted. Up to 60% glucose conversion was achieved, based on the available cellulose values without pretreatment. The report presents a scheme for a continuous, production-scale acid hydrolysis-fermentation facility based on a waste cellulose feedstock for production of fuel-grade ethanol.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and pubic health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small business in handling their wastes responsibly and economically.

In the past decade, interest in the possible industrial use of waste biomass for recovery of materials and energy has been greatly enhanced by the convergence of two apparently unrelated problems, namely the steadily rising price of fossil fuels and the ever increasing magnitude of the solid waste disposal problem. The subsequent EPA sponsored research describes a both technically and economically attractive approach for the cost effective recovery of solid wastes energy and materials especially for the cellulose which constitutes a major portion of solid wastes.

The information contained herein will be of interest to those designers or users who are contemplating or working with a system similar to this recovery system. Requests for further information regarding the production and utilization of refuse-derived fuel should be directed to the Thermal Destruction Branch, HWERL, Cincinnati.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

CONTENTS

FOREWORD ii
LIST OF FIGURES v
LIST OF TABLES vii
ACKNOWLEDGEMENT viii
ABSTRACT ix

1. INTRODUCTION 1
2. SUMMARY 6
3. DESCRIPTION OF STUDY 9
4. RESULTS AND DISCUSSION 11
   A. BATCH HYDROLYSIS 11
      Introduction 11
      Accessibility -- Need for Pretreatment 12
      Pretreatment Procedures 12
      Batch Reactors 12
      Experimental Method 16
      Experimental Results 16
      Conclusions 29
   B. CONTINUOUS HYDROLYSIS 30
      Advantages of a Continuous Process 30
      Equipment Selection 30
      The Problems of a High Pressure Flow Reactor 31
      Feedstock Handling 31
      Feeding 32
      Dewatering 32
      Dynamic Plug: Formation and Stability 32
      Discharge Methods 38
      Collection 41
      Instrumentation 42
      Steam Supply 42
      Energy Optimization 43
      Wear and Corrosion Monitoring 44
      Residence Time Distribution 45
      Blockage-Clearing Techniques 45
      Pulp Hydrolysis Results 46
      Sawdust Hydrolysis Results 46
      Transfer to a Larger Facility 50
   C. SUMMARY 50

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

Contents (Cont'd)

5. GLUCOSE UTILIZATION 56
    A. PRODUCT ANALYSIS 56
    B. GLUCOSE RECOVERY 57
    C. FERMENTATION AND BIOCONVERSION 60

6. MAXIMUM USE OF FEEDSTOCK 62
    A. MATERIAL FLOW AND HEMICELLULOSE UTILIZATION 62
    B. ENERGY BALANCE 65
    C. LIGNIN UTILIZATION 65

7. ENVIRONMENTAL CONSIDERATIONS 70

8. ECONOMICS 77
    A. SCALE-UP TO INDUSTRIAL FACILITY 77
    B. INVESTMENT COSTS AND RETURN ON INVESTMENT 78
    C. MUNICIPAL SOLID WASTE AS FEEDSTOCK 78

9. REFERENCES 84

APPENDIX A -INITIAL EXTRUDER TRIALS AT WERNER & PFLEIDERER CORP. 88
    FEEDING 88
    PROCESSING 88
    DISCHARGE 89
    ACID INJECTION 89
    CONCLUSIONS 89

APPENDIX B - MOBILE HYDROLYSYS UNIT PROPOSAL 90

APPENDIX C - SOLAR STEAM GENERATION PROPOSAL 93

APPENDIX D -NYU BENCH-SCALE FERMENTATION TRIALS 95
    YEAST 95
    SUBSTRATE PREPARATION 95
    FERMENTATION PROCEDURE 95
    ACCLIMATION PROCEDURE 96
    RESULTS 96

APPENDIX E - UNIVERSITY OF GEORGIA BIOCONVERSION TRIALS 99

APPENDIX F - LOUISIANA STATE UNIVERSITY BIOCONVERSION TRIALS 100

APPENDIX G - RECYCLING OF CELLULOSE 101

APPENDIX H - ORGANIC ACID CATALYSTS 102

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BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS

LIST OF FIGURES

Figure Page

1. Waste Cellulose Utilization Routes 2
2. Possible Routes to Petrochemicals from Cellulosic Wastes 3
3. Cellulose to glucose process 8
4. Batch Scale Acid Hydrolysis Reactor; 1-Liter System 13
5. Batch Scale Acid Hydrolysis Reactor; 5-Liter System 14
6. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 0.28% sulfuric acid and 450 F (232 C) 17
7. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 0.58% sulfuric acid and 450 F (232 C) 18
8. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 0.656% sulfuric acid and 450 F (232 C) 19
9. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 1.15% sulfuric acid and 450 D (232 C) 20
10. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 1.29 % sulfuric acid and 450 F (232 C) 21
11. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 1.70% sulfuric acid and 450 F (232 C) 22
12. Glucose yield vs reaction time for acid hydrolysis of N.Y. Times at 2.24% sulfuric acid and 450 F (232 C) 23
13. Glucose yield vs reaction time for acid hydrolysis of hydropulped Garden State paper at 450 F (232 C) 24
14. Glucose yield vs reaction time for acid hydrolysis of Garden State paper; hydropulped and irradiated at two dosages 25
15. Glucose yield vs reaction time for acid hydrolysis of Garden State paper at 450 F (232 C) for various pretreatments 26
16. Glucose yield vs reaction time for acid hydrolysis of hydrogen peroxide pretreated hydropulped Garden State paper 27
17. Glucose yield vs reaction temperature for acid hydrolysis of hydrogen peroxide pretreated hydropulped Garden State paper. Acid - 0.87%. Residence time = 10 sec. 28
18. Schematic of the New York University Hydrolysis System: Arrangement for "Wet" Feedstocks 34

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

List of Figures (Cont'd)

Figure Page

19. Schematic of the New York University Acid Hydrolysis System: Arrangement for "Dry" Feedstocks 34
20. Typical Extruder Screw Configuration (with permission of WPC) 36
21. Hydraulic Actuator System for Ball Valve Discharge 39
22. Ball valve operation; material discharged, pressure retained 40
23. Alpha-Cellulose to Glucose Conversion Yield vs Acid Concentration, Newsprint Pulp 48
24. Alpha-Cellulose to Glucose Conversion Yield vs Acid Concentration, Sawdust 49
25. Yield vs Residence Time, Eastern White Pine 51
26. Yield vs Acid Concentration, Eastern White Pine 52
27. Yield vs Reaction Temperature, Eastern White Pine 53
28. Floor plan of New York University Continuous Acid Hydrolysis Facility 54
29. Centrifuge: Final glucose concentration vs % recovery 58
30. Material Flow for Single-Stage Process 63
31. Material Flow for Two-Stage Process 64
32. Energy Balance for NYU Acid Hydrolysis Process 66
33. Effect of market price of co-produced lignin on ethanol selling price 68
34. Material Balance 71
35. ROI Sensitivity Analysis 82
D-1. Fermentation of Aspen Hydrolyzate 97
H-1. Hydrolysis with Organic Acids 103

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TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
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PAGE NUMBER
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LIST OF TABLES

Table Page
1. Analysis of Wiley Mill Ground Newsprint 15
2. Analysis of Industrially Ground Newsprint 15
3. Results in Extruder Hydrolysis of Paper Pulp 47
4. Conversion Yield vs Acid Concentration For Continuous Hydrolysis of Sawdust 50
5. Separation Trials on Sugar Maple Hydrolyzate 59
6. Analysis of Mixed Hardwood Sawdust (55) 62
7. Market Sizes and Values of Thermosetting Resins at Various Replacement Levels with Lignin 69
8. Material Balance 72 - 74
9. Particulate and Gaseous Emissions for Direct Combustion of Biomass Residues Compared with Coal Combustion Kg/10^6 BTU 75
10. Composition of Stillage 76
11. Capital Costs 79
12. Production Costs 80
13. Return on Investment 81
14. Effect of Feedstock Cost and Electricity Sale 83
B-1. Mobile Acid Hydrolysis Unit Based on WPC ZDS-K83 92
D-1. Fermentation of New York University Hydrolyzate 97
G-1. Effect of Recycling on Glucose Yield for Dilute Sulfuric Acid Hydrolysis at 450 F 101
H-1. Maleic Acid Catalyzed Hydrolysis of Waste Cellulose (Feedstock: Garden State Paper Co., Used Newspapers) 102

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ABSTRACT

This report describes a 5-year investigation on the conversion of cellulosic materials and wastes to glucose, potentially an enormous source of ethanol and a wide range of petrochemicals. Employing a co-rotating twin-screw extruder as reaction vessel, the New York University (NYU) process achieves a fully continuous dilute-acid hydrolysis at temperatures around 240 C and residence times of 5 to 10 seconds. It handles feedstocks ranging from waste paper pulp at 10% solids to corn bran to dry hardwood sawdust at 95% solids without pretreatment and gives good conversion yields, around 60% of the available cellulose, with low energy consumption.

Using a full engineering feasibility study based on accurately measured materials and energy balances, economically attractive projections are given for scale-up from the 2 ton per day pilot plant, which has operated for three years, to a full scale commercial plant producing 25 million gallons of ethanol per year.

Also given is an account of early NYU work on small batch versions of the hydrolysis process with emphasis on various pretreatments to increase cellulose accessibility and thus glucose yields, an emphasis which was later rendered unnecessary by the high efficiency of the extruder conversion. Descriptions are given of work on separation of the product, analytical techniques, studies on fermentation and bioconversion to methane and utilization of the hemicellulose and lignin fractions of the plant material. Environmental considerations are discussed, as well as a proposal for a mobile version of the NYU process.

This report was submitted in fulfillment of Cooperative Agreement EPA-R805239-030 by the Department of Applied Science, New York University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 25, 1977 through March 31, 1981.

SECTION 1

INTRODUCTION

Interest in the possible industrial use of waste biomass for recovery of materials and energy has been greatly enhanced by the convergence of two apparently unrelated problems -- the inevitably rising price of fossil fuels and the ever-increasing magnitude of the solid waste disposal problem (1,2,3). Current methods of dealing with these solid wastes are inadequate for cost-effective use of recovered energy and materials -- especially for the cellulose, which constitutes a major portion of solid wastes (4-11). Conversion of waste cellulose to glucose by means of acid hydrolysis is a promising approach to this growing but underutilized material resource. As shown in Figures 1 and 2, the glucose from cellulosic wastes could be used to manufacture many volume chemicals presently obtained from petrochemical feedstocks (2).

The potential quantities of chemical feedstocks, etc., that could be obtained from waste cellulose are substantial (2,10). Assuming a realistic 12% available cellulose in the wastes and only 16% conversion to ethylene, the estimated 1550 million tons of farm waste alone would yield more than 30 million tons of ethylene annually -- twice the U.S. consumption of this basic chemical building block in 1978. The economic feasibility of using waste cellulose depends greatly, of course, on both waste collection and processing conversion costs, as well as on the quantities and values of the various end products obtained.

Acid hydrolysis of cellulose has been extensively studied for the better part of a century, particularly in connection with manufacturing ethanol from wood wastes. The discovery that cellulose can be hydrolyzed in acid solutions and converted to its monomer, glucose, was first reported by Bracconnot 160 years ago, in 1819 (18). The reaction has been experimentally investigated ever since then, mostly on a strictly empirical basis, in order to develop a cost-effective process for producing sugar from wood wastes and other sources of waste cellulose.

Research and development on the acid hydrolysis of wood wastes was particularly active during the first part of this century, both in the U.S. and Western Europe (12,13). These acid hydrolysis studies went far beyond the laboratory scale, up to the construction and operation of production facilities for glucose and ethanol. The U.S.S.R. and Japan have also been very active in the field of wood saccharification.

While the acid hydrolysis of cellulose is heterogeneous, it can be regarded as a homogeneous reaction provided that the cellulose reactant is

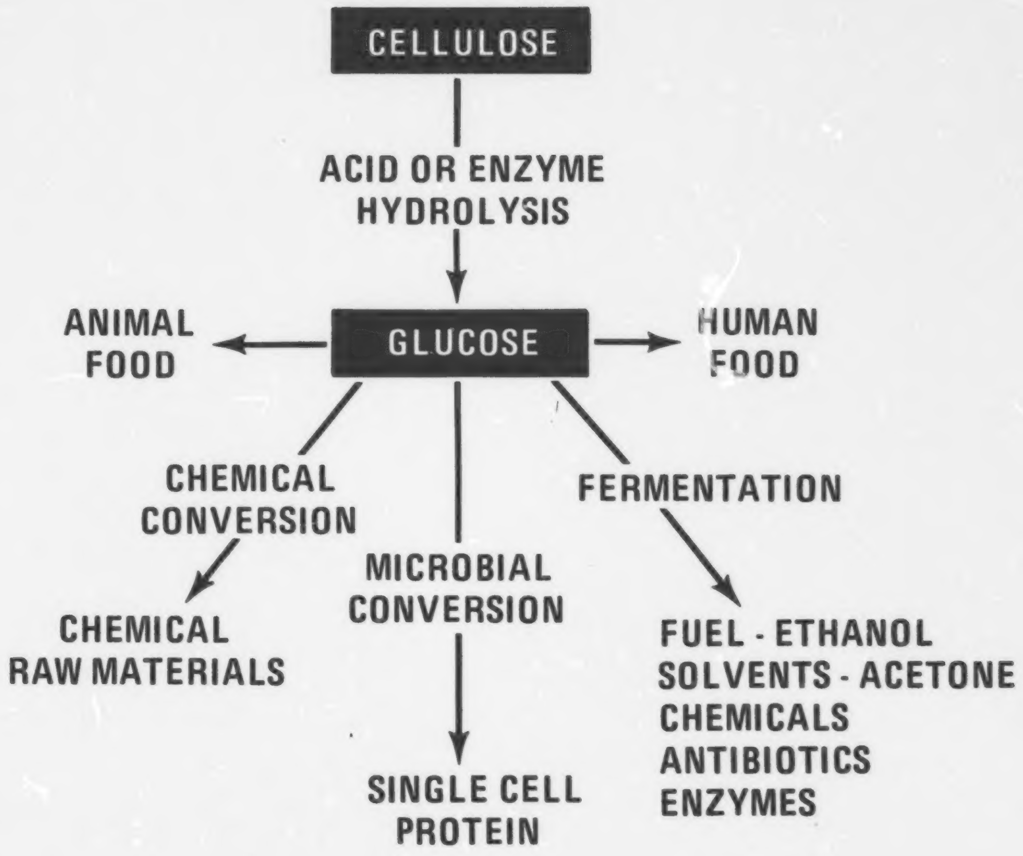
CELLULOSE
ACID OR ENZYME HYDROLYSIS
GLUCOSE
ANIMAL FOOD
HUMAN FOOD
CHEMICAL CONVERSION
CHEMICAL RAW MATERIALS
MICROBIAL CONVERSION
SINGLE CELL PROTEIN
FERMENTATION
FUEL - ETHANOL
SOLVENTS - ACETONE
CHEMICALS
ANTIBIOTICS
ENZYMES

FIGURE 1: Waste Cellulose Utilization Routes

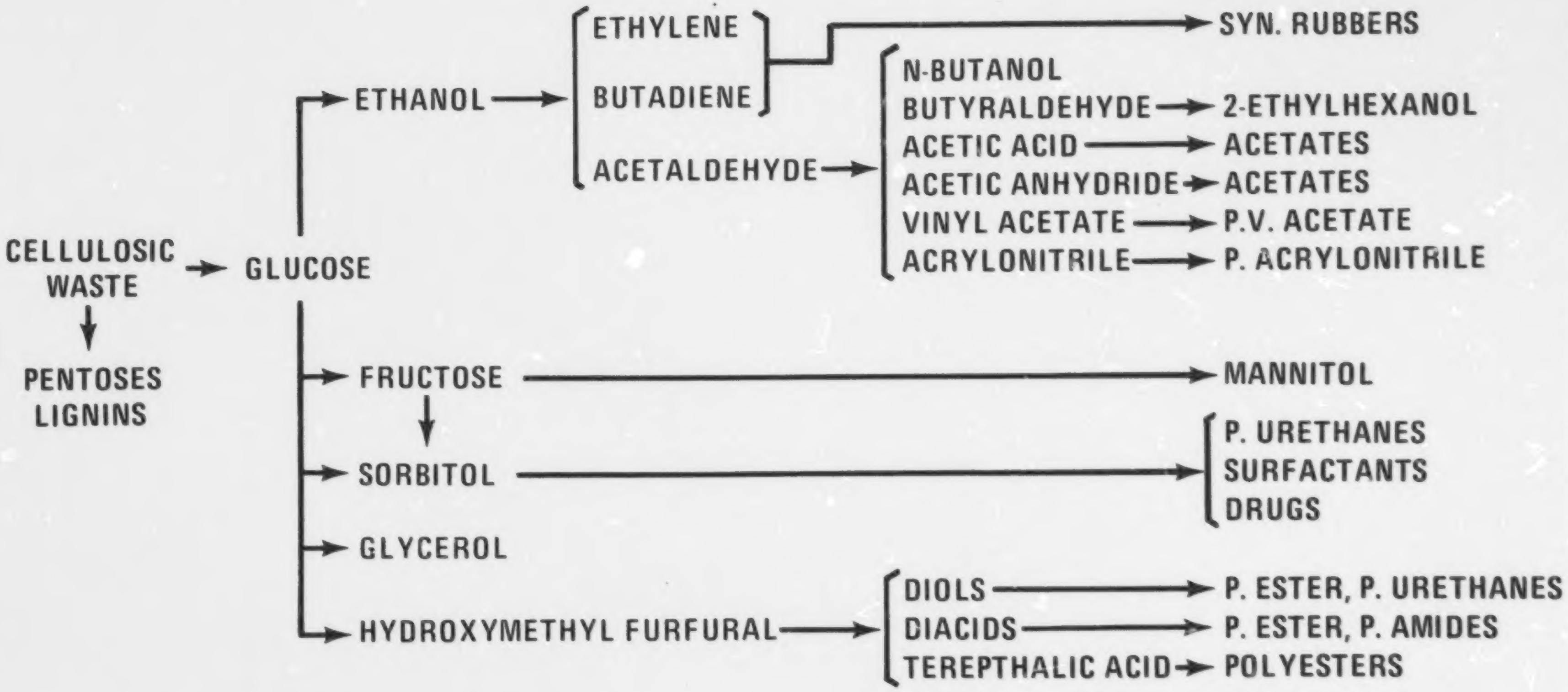
CELLULOSIC WASTE
GLUCOSE
PENTOSES LIGNINS
ETHANOL
ETHYLENE
BUTADIENE
ACETALDEHYDE
SYN. RUBBERS
N-BUTANOL
BUTYRALDEHYDE
2-ETHYLHEXANOL
ACETIC ACID
ACETATES
ACETIC ANHYDRIDE
ACETATES
VINYL ACETATE
P.V. ACETATE
ACRYLONITRILE
P. ACRYLONITRILE
FRUCTOSE
MANNITOL
SORBITOL
P. URETHANES
SURFACTANTS
DRUGS
GLYCEROL
HYDROXYMETHYL FURFURAL
DIOLS
P. ESTER, P. URETHANES
DIACIDS
P. ESTER, P. AMIDES
TEREPTHALIC ACID
POLYESTERS

FIGURE 2: Possible Routes to Petrochemicals from Cellulosic Wastes

dispersed in the form of fine particles, e.g. 200 mesh or less. A kinetic scheme for the acid hydrolysis of crystalline wood cellulose was proposed by Lüers (38) and then Saeman (14) more than 30 years ago. This scheme was used to effectively model the hydrolysis of cellulose in wood chips and cotton linters.

Converse, Grethlein, and later Fagan et al., applied Saeman's model to describe the formation of glucose from commercially available waste paper (15-17). Porteous predicted a maximum sugar yield of 55% with 0.4% acid at around 230 C. The Fagan experiments were carried out with rather small samples (0.5 gms) of ball milled Kraft paper, and verified Saeman's predictions. Such kinetic studies are now deemed of considerable value for the development of improved process designs and economic data of waste cellulose to glucose and/or ethyl alcohol production facilities (16,17).

The kinetically predicted maximum sugar yields assume that the cellulose reactant has appropriate chemical reactivity for the acid hydrolysis. The technical problems of cellulose hydrolysis are to a great extent due to the fact that this is not the case. The lack of an adequate amount of chemical reactivity in cellulose is called lack of accessibility. This is related to the highly inert character and crystalline organization on a molecular level of the high molecular weight cellulose, and also to the presence of lignin. Hydrogen bonding plays a very important role in the structure of cellulose, and may be a key factor in explaining its chemical inertness.

Over the years, a very extensive amount of R&D has been aimed at the development of cellulose pretreatments which are both technically effective and economically viable (21,22). The basic approach has been to reduce the crystallinity and disrupt the hydrogen bonding, thus rendering the cellulose more accessible to hydrolytic depolymerization reactions. This should make it possible to approach the predicted glucose yields more closely. Many different pretreatments have been proposed and a considerable number of them have been experimentally investigated, including grinding, high energy irradiation, and exposure of the cellulose to various chemicals.

Employment of high energy ionizing radiation has been shown to be at least equally as effective as widely used grinding pretreatments when the cellulose is exposed to dosages on the order of 100 megarads (14). Sugar yields as high as 70% based on the available cellulose content have, for example, been reported. Such large dosages of ionizing radiation are, however, too high for industrial usage. Thermal and radiation treatments have been combined to allow lower radiation dosage levels, which are more acceptable economically (22). Various chemical treatments have been investigated as well, with relatively little success (21).

Development of lower cost pretreatment technology, such as would produce substantial crystallinity reductions for improving the accessibility of cellulose, is recognized as a prime consideration for an economically as well as technically effective waste cellulose to glucose conversion process. This pretreatment must furthermore be combined with a high productivity, high yield acid hydrolysis process so as to optimize the conversion of the pretreated waste cellulose to glucose.

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Experiments carried out over the past few years at New York University's laboratories have resulted in the development of a new high temperature acid hydrolysis process that overcomes the major problems that have been associated with this reaction. The important features of this process include the development of a cost-effective pretreatment for the waste cellulose that enhances its reactivity in an acid medium, and the establishment of reaction conditions that can produce yields on the order of 60% (based on the available cellulose values) in very short periods of time. Dilute sulfuric acid was used in the aqueous hydrolysis medium.

This rapid high-temperature acid hydrolysis process has been successfully scaled up, first to a 1-liter and then to a 5-liter stirred autoclave reactor. The larger reactor and associated equipment have been operated on a batch basis very satisfactorily for prolonged periods, and the glucose yields obtained have been reproducibly consistent. The equipment and utility requirements, as well as glucose production costs, have been investigated for scaled-up production operations. These studies have shown the desirability of a continuous acid hydrolysis process comprising a waste cellulose pretreatment followed by a rapid high-temperature hydrolysis for cost effective glucose production on a larger scale.

Designing a continuous 1-ton/day waste-celllulose-to glucose pilot plant facility was the next logical step. Investigations of various types of equipment for the hydrolysis conversion led to the concept of using a screw-type conveyor, mixer, and reactor device for hydrolyzing waste cellulose in a slurry form. After some exploratory experiments, the equipment selected was a Werner & Pfleiderer ZDS-K53 Co-rotating Twin Screw Extruder.

A three year program was implemented by an EPA Cooperative Agreement, and has now been successfully completed. New York University (NYU) activities were concentrated on the design of the 1-ton/day pilot plant unit, the necessary detailed specifiction of equipment and materials, their procurement, preparatory work necessary for equipment installation, and equipment shakedown. This work was carried out at the Antonio Ferri Labs of NYU in Westbury, Long Island.

For continuous processing, the extruder had to be coupled with a mechanism for feeding the various cellulosic feedstocks, together with a system for discharging the products while maintaining high pressure and temperature in the reaction zone. Two main types of feedstock were hydrolyzed, namely used newspaper and sawdust. The effects of pertinent reaction variables on the glucose yield obtainable from these wastes were studied. Separation of the glucose from unconverted material and other reaction products was also investigated. Exploratory studies were conducted on the acid hydrolysis of alternative waste cellulose sources, especially agricultural residues. The results of these investigations are the subject of this final report.

SECTION 2

SUMMARY

The principal result of this study was the development of a continuous process concept from commercially available equipment for the dilute acid hydrolysis of waste cellulose, a schematic of which is given in Figure 3. Batch hydrolysis studies carried out for two years gave extensive data on which the continuous process was based.

Pretreatment studies led to the belief that to gain cellulose accessibility, one needed to impart energy in some form to the cellulose. A combination treatment of high energy electron beam irradiation in conjunction with hydropulping was seen to be more effective while less costly than mechanical treatments. Results of chemical pretreatments were inconclusive. Hydrolysis experiments made with organic acids in place of sulfuric acid to reduce corrosion proved effective, but too expensive for serious commercial consideration. The emphasis on pretreatments diminished as development of the continuous reactor proceeded.

Based on plant trials (described in Appendix A), a decision to use a commercially available co-rotating twin-screw extruder (Werner & Pfleiderer Corporation, Ramsey, NJ: Model ZDS-K53) was made because of its modular design and inherent versatility. The problem of forming a high pressure reaction zone in a flow system was the key issue. This involved creating an upstream seal while material is fed in, and a downstream seal while material is discharged. The upstream dynamic seal was generated by compacting material (cellulosic feed) using either reverse pitch screw elements or ultimately by inserting screw bushing "blanks" with no conveying screw crests. The length of the upstream seal could be controlled by changing the length of the crestless elements. It is best described as a "dynamic plug".

The downstream seal/discharge was accomplished by the design of a rapid-acting ball valve which discharged semi-continuously while both the speed of the ball as well as the frequency of the cycle (for example, a 1/30 second discharge every 15 seconds) could be controlled. While this system showed the feasibility of the extruder reactor concept, the pulsed nature of this process in some cases caused severe surges of torque loading on the extruder. A truly continuous discharge was needed, and was ultimately developed utilizing an orifice. Several alternative discharge designs which were developed are also described.

The next problem that surfaced was the need for better temperature control and a high pressure steam generator with a larger capacity. The balancing of feed rates, dewatering effects on certain feeds, uncertainties

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of plug formation upstream causing blow-backs, the control of acid concentration, etc., were just some of the issues that were studied in the development of this expertise. It was soon clear that the number of process variables to be controlled would require automatic data compilation, and ultimately automatic feedback-coupled control. This work is still under development, as is optimization of several other aspects of the process. However, at the culmination of the project period, the feasibility of continuously hydrolyzing various cellulosic feeds at high glucose yields using the extrusion technique had been clearly proven. Additionally, the capability of handling high solids feeds resulting in a product with high glucose content was established for the extruder.

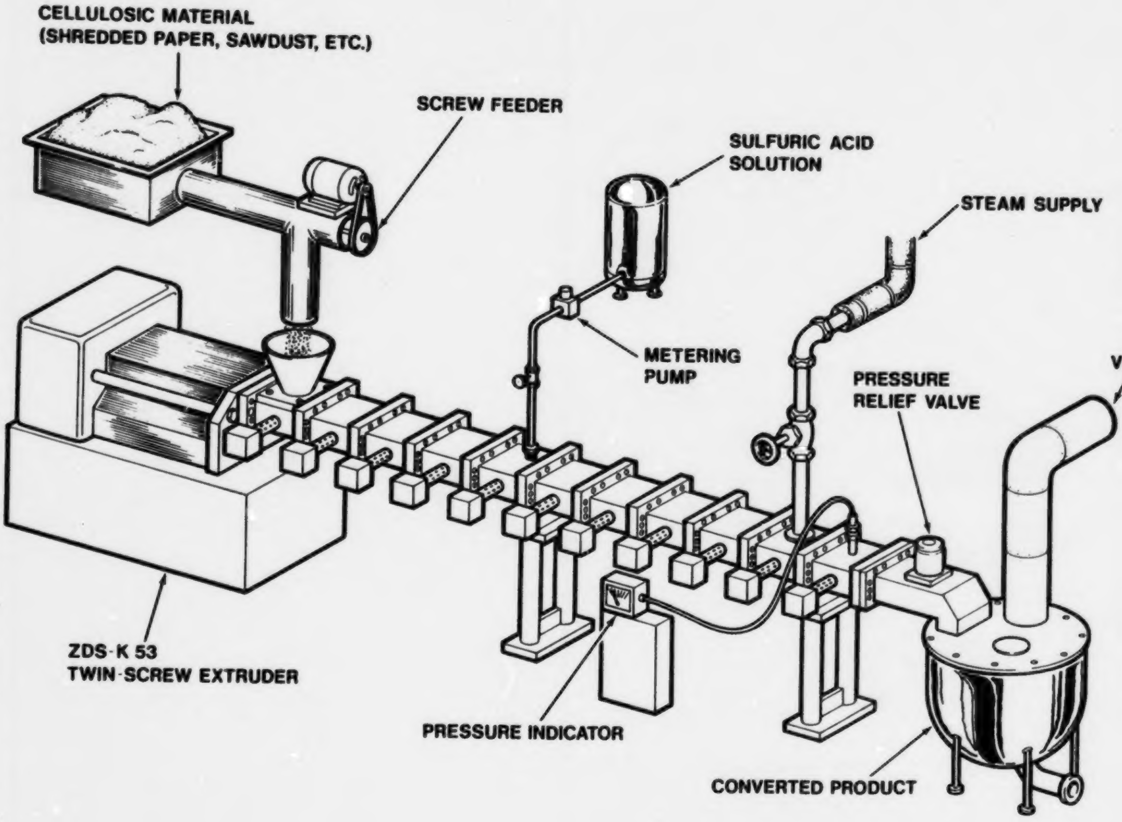
The studies on process development branched out to issues of handling the product once out of the reactor. These issues included separation, fermentation, and analysis; further subjects included environmental impact and overall process economics.

Trial separation studies were done using a semi-continuous centrifuge (Lavin Model 1120A). It was soon evident that hydrolysis reaction conditions played an important role in product separability. If the cellulose were "under-reacted", the product contained a high fiber content and subsequently the water-soluble fraction was difficult to remove. At best, a filter cake with 30% solids was produced in the lab centrifuge. Further washing of the cake to extract residual sugars caused excessive dilution. However, under more severe reaction conditions where more of the fiber properties of the cellulose were destroyed, it was shown that the product could be separated more effectively and centrifuge cakes of 50-70% solids content could be produced.

Fermentation studies on the glucose initially concentrated on the generation of methane. A subcontract with the Louisiana State University Microbiology Department was undertaken. The basic findings of the study were that inhibitory agents existed in the hydrolyzate which interfered with the digestion. No attempt was made to acclimate the methanogens to this environment. Subsequent studies in the NYU Labs on yeast fermentation of the glucose to ethanol, using a gradual acclimation technique, were quite successful (see Appendix D).

Early analyses done at NYU and commercially for NYU were wet-chemistry reducing-sugar tests which were subject to byproduct interferences and could not properly distinguish between the various reducing monosaccharides. High pressure liquid chromatography (HPLC) was clearly the best method for separating and analyzing carbohydrate mixtures, but implementation was limited by the rate of development of dedicated carbohydrate chromatographic columns; the best-demonstrated expertise in this field was that of Waters Associates, (Milford, Mass.), and this equipment was used in subsequent NYU analyses. Methods were evolved not only for monosaccharides, but for oligosaccharides and breakdown products also, thus allowing detailed evaluation of the efficiency of the process.

Environmental studies done indicate no significant adverse impact. Conventional water and air treatments are adequate. Economic analyses and a full engineering feasibility study have been carried out for the production of fuel grade ethanol for gasohol from glucose, and indications are that such a process would be competitive with ethanol from grain under current market conditions.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SCREW FEEDER
SULFURIC ACID SOLUTION
STEAM SUPPLY
METERING PUMP
PRESSURE RELIEF VALVE
VENT
ZDS-K 53 TWIN-SCREW EXTRUDER
PRESSURE INDICATOR
CONVERTED PRODUCT

Figure 3. Cellulose to glucose process.

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SECTION 3

DESCRIPTION OF STUDY

As originally conceived, the EPA-sponsored program at NYU was to investigate novel approaches to utilization of cellulosic wastes for the production of energy. More specifically, it was determined that high temperature dilute acid hydrolysis was of particular interest, with emphasis, at least initially, on pretreatment of feedstocks to maximize cellulose accessibility for efficient conversion to glucose. The feedstock selected was dry waste paper and paper pulp, which were to simulate a feedstock derived from municipal solid waste.

During the initial stage of the project, batch hydrolysis experiments were designed in which two differently-sized reactors were tested (first 1-liter, and later 5-liter). These experiments represented a scale-up of previous researchers' kinetic modelling experiments. Various pretreatments were investigated, including mechanical grinding, pulping, and high energy electron beam irradiation. Specific chemical treatments were also evaluated in terms of their effect on cellulose accessibility. Since the sulfuric acid catalyst was seen to present potential corrosion problems, some experiments were done using organic acids as less corrosive substitutes.

After scaling-up from the 1-liter to the 5-liter reactor, it was soon evident that, because the optimal requirements of this process include rapid heat-up, short residence time, and very precise control of reaction conditions, it is not amenable to a batch operation. A concept was developed for carrying out cellulose hydrolysis on a continuous basis, using a plastics extruder as a reaction vessel.

The balance of the project period (three years) was concerned with designing, setting up, and operating a pilot plant. The first year of this phase of the project involved the specification, design, procurement, and shake-down of the reactor and all of the appropriate ancillary equipment. The second and third years dealt with various improvements to the process, and the identification of numerous engineering problems and their subsequent solution.

As actual operation of the plant proceeded, it became apparent that the efficiency of the extruder for cellulose conversion is sufficiently high that pretreatment of the feedstock is not necessary. The feedstock of choice was a waste newspaper pulp (supplied by Garden State Paper Co., Garfield, NJ), and although some samples were subjected to pretreatment via irradiation, this aspect of the study was de-emphasized.

In the reactor itself, the following aspects of operation were addressed:

- feeding of cellulosic waste into the high pressure reaction zone,
- precise control of reaction pressure, temperature, and residence time,
- addition of acid catalyst,
- addition of high pressure steam,
- minimization of moisture content passing through the reaction zone,
- discharge of product from the high pressure reaction zone.

A vessel was designed and constructed for collecting and sampling the product as it flashed from the reactor, and thus a continuous conversion system that could hydrolyze paper pulp was completed about 1½ years into the 3 year pilot plant study.

In addition to reactor design, the problems of product (glucose) separation from the reaction mass as well as its analysis were studied. Early tests utilized an outside commercial analytical facility, but the results were unsatisfactory, and the need for an on-site analytical capability was soon evident; this was steadily developed. Investigation of techniques for separation of the product sugar from the reaction mass led to the acquisition of a lab centrifuge (semi-continuous), with the aim of obtaining additional information on separation efficiency.

By the onset of the third year, sawdust had been successfully hydrolyzed. This was seen as a major advance, since the ability to handle a low-moisture cellulosic feedstock without first forming a slurry meant that the level of water carried with the reaction mass was significantly decreased, and thus the energy requirement was reduced substantially. Sawdust as a feedstock naturally required redesign of the feeding section of the process. Also, the product was a more complex mixture of sugars requiring improved analytical capabilities.

Work during the final year of this study was aimed at improving the versatility, reliability, and efficiency of the extruder system. Bacterial fermentation studies were carried out at Louisiana State University for conversion of glucose to methane; yeast fermentation studies were commenced at NYU for conversion of glucose to ethanol. Materials and energy balances were developed and used as a basis for economic analyses and projections, and environmental impacts were studied.

What follows is an account of the major results of this five year program. For completeness, appendices are added which reflect some of the subsequent developments of work commenced during this period. Included are results obtained under contractual agreements principally with the Department of Energy through the Solar Energy Research Institute, and the New York State Energy Research and Development Authority.

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SECTION 4

RESULTS AND DISCUSSION

A. BATCH HYDROLYSIS

Introduction

This section describes the NYU research and development activities on a laboratory scale of a process for the acid hydrolysis of waste cellulose to glucose. The waste cellulose feedstock employed in these studies was primarily used newspapers: dry sheets of the NY Times were used in some experiments, while the majority employed pulp of measured solids concentrations, which was obtained from the Garden State Paper Co., Garfield, NJ. The experimental work comprised an evaluation of various pretreatments for enhancing the accessibility of waste cellulose to acid hydrolysis; the determination of the optimum hydrolysis reaction conditions so as to maximize the sugar yields; and techniques for glucose recovery from the hydrolysis reaction products, including recycling of unreacted feedstocks.

Accessibility -- Need for Pretreatment

Some of the technical problems of hydrolysis center around the unreactive nature of the resource. This is due to the inert character and crystalline organization on a molecular level of the high molecular weight cellulose, and also to the presence of lignin. As the crystalline cellulose polymer network must be penetrated for hydrolysis, this "accessibility" problem has been found to be particularly serious for the enzymatic process, on account of the much larger size of an enzyme molecule as compared to the hydrated proton involved in the acid process. Other problems relate to increasing the waste cellulose concentration in the slurries being hydrolyzed and the nature of the reaction conditions, particularly reaction time, which for optimal conversion with enzymatic hydrolysis can be on the order of as much as two days.

Effective pretreatment of waste cellulose feedstocks to enhance cellulose reactivity was considered essential for obtaining high glucose yields. The technically most satisfactory pretreatment previously found was ball milling, which reduces the crystallinity and particle size of the cellulose and increases its bulk density (37). Thus more cellulose is made available for saccharification and glucose yields are significantly enhanced. Ball milling is however an expensive process, and adds so much to the hydrolysis cost as to make the process economically prohibitive. Other pretreatments which have been experimentally investigated with varying degrees of technical success include exposure of the cellulose feedstock to ultraviolet (UV) or

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electron beam (EB) radiation, treatment with chemicals which swell or otherwise affect the cellulose structure, and various mechanical, thermal processes (22).

Over the course of the first 2½ years of this study, several pretreatments for waste newsprint prior to hydrolysis were comparatively evaluated. These included: 1) Wiley Mill grinding, 2) industrial grinding, 3) hydropulping (laboratory simulation), 4) electron beam irradiation, and 5) hydrogen peroxide degradation. A short description of the procedures employed is given below.

Pretreatment Procedures

Wiley Mill Grinding: NY Times was hand torn into 2" rectangles, then fed into a standard #3 laboratory size Wiley Mill fitted with a welded brass screen plate with 1/8" round perforations. The paper was passed through the machine once and analyzed as per Table 1.

Industrial Grinding: Newsprint was passed once through a standard industrial Williams Hammer Mill Shredder, equipped with a 1/8" round hole perforated screen plate. Table 2 shows the results.

Hydropulping: Fifty gram samples of Garden State Paper were weighed out and hand torn into a one gallon Waring Blender with 2450 gms of water to make a slurry of approximately 2% solids. The blender was run at high speed for 15 seconds. The excess water was then filtered off with a Büchner funnel to make a higher solids slurry prior to the hydrolysis experiment (10% solids nominal).

Irradiation: Fifty gram samples of Garden State Paper were hydropulped and filtered to a preset slurry concentration, then sealed in plastic bags. These samples were exposed to high energy electrons at a specified dosage (10 and 20 megarads). The irradiation equipment used was that of Radiation Dynamics Inc., Plainview, NY.

Hydrogen Peroxide: Fifty gram samples of Garden State Paper were hydropulped with 2450 gms of 0.1 M acetate buffer (pH = 4.2) containing 2.31 gm $FeSO_4$. The slurry was secured in a plastic bucket and equilibrated in a 30 C water bath. Then 82.5 gm of 30% H_2O_2 was added and the reaction begun with constant agitation. The runs were 16-18 hrs in duration, after which the peroxide was dissipated and the treated newspaper was filtered, washed, and refiltered before being subjected to acid hydrolysis.

Batch Reactors

Hydrolysis batch experiments were initially run in a 1-liter reactor (Figure 4), and in due course scaled up to a 5-liter reactor (Figure 5). These reactors were both stainless steel, stirred autoclaves which were instrumented for reading temperatures and pressures. Acid solutions were injected from an external bomb after the reaction mass was heated to the appropriate temperature. The reactors were fitted with quick-acting discharge valves and properly-sized collection vessels. In the early experiments using

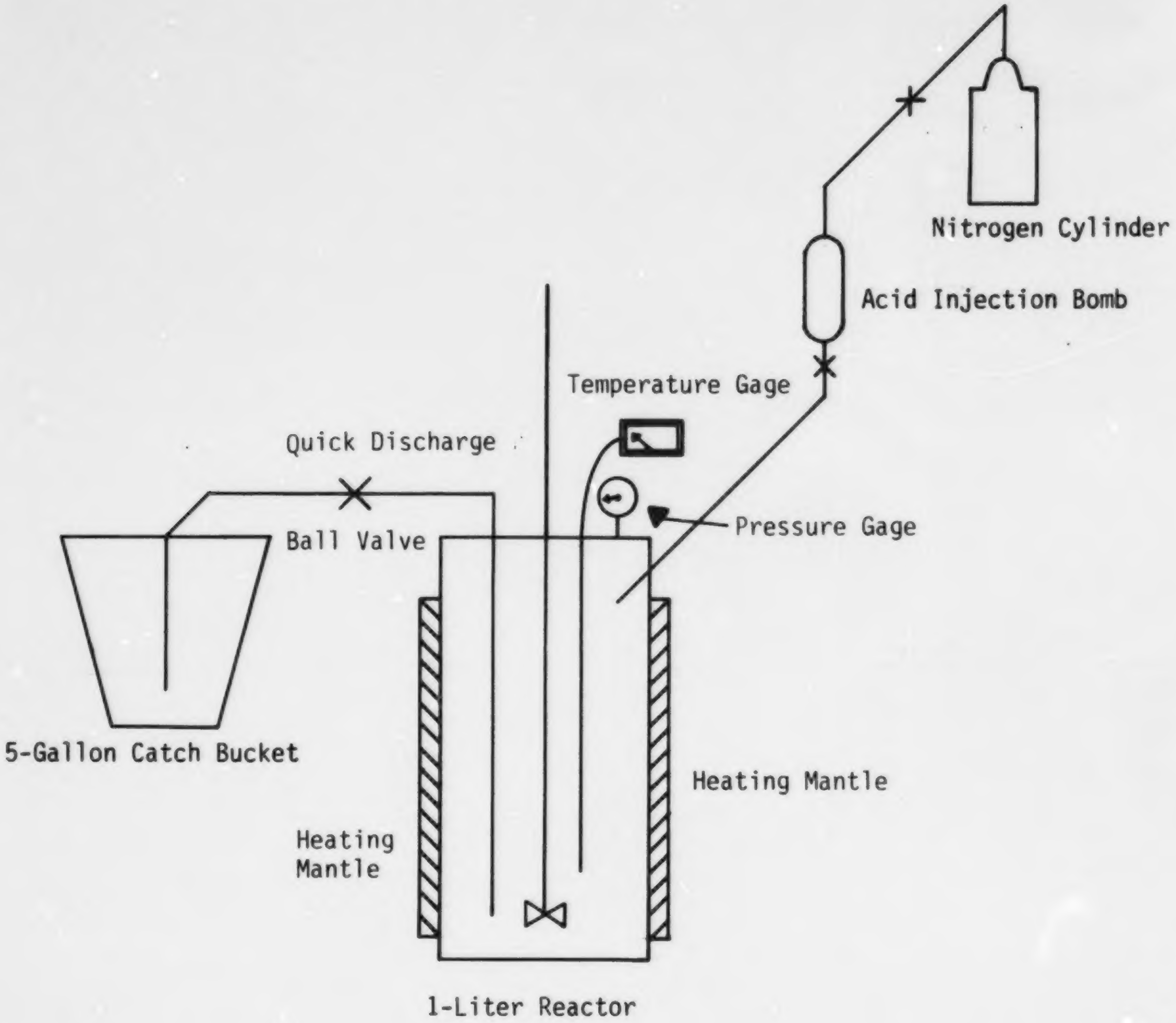
Nitrogen Cylinder
Acid Injection Bomb
Temperature Gage
Quick Discharge
Ball Valve
Pressure Gage
5-Gallon Catch Bucket
Heating Mantle
Heating Mantle
1-Liter Reactor

FIGURE 4: Batch Scale Acid Hydrolysis Reactor; 1-Liter System

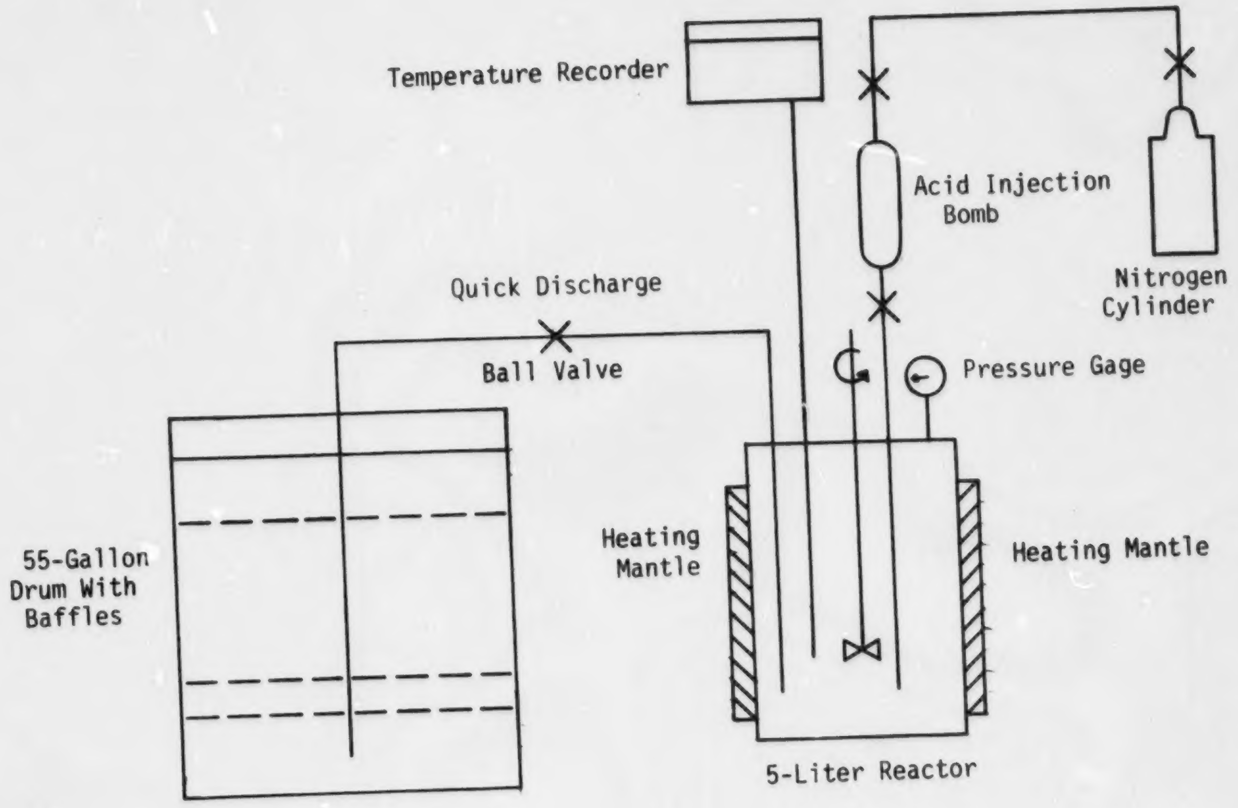
Temperature Recorder
Acid Injection Bomb
Nitrogen Cylinder
Quick Discharge
Ball Valve
Pressure Gage
55-Gallon Drum With Baffles
Heating Mantle
Heating Mantle
5-Liter Reactor

FIGURE 5: Batch Scale Acid Hydrolysis Reactor; 5-Liter System

TABLE 1. ANALYSIS OF WILEY MILL GROUND NEWSPRINT

(#3 standard Wiley Mill with 1/8" round hole perforated screen plate.)

Sieve #	Pore Size (inches)	% Material Which Does Not Pass
18	0.0394	9.6
20	0.0331	15.2
25	0.0280	12.8
35	0.0197	24.3
40	0.0165	5.6
45	0.0138	5.5
50	0.0117	5.1
60	0.0098	2.5
100	0.0059	16.0
Fines		3.4
	Total	100.0

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TABLE 2. ANALYSIS OF INDUSTRIALLY GROUND NEWSPRINT

(Williams hammer mill shredder with 1/8" round hole perforated screen plate.)

Sieve #	Pore Size (inches)	% Material Which Does Not Pass
10	0.0787	40.0
14	0.0555	5.6
18	0.0394	6.4
20	0.0331	3.4
25	0.0280	4.6
35	0.0197	6.4
40	0.0165	4.0
45	0.0138	5.3
50	0.0117	4.7
60	0.0098	7.5
100	0.0059	11.1
Fines		1.0
	Total	100.0

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the 1-liter reactor, a known amount of ice was put in the collection vessel to quench the reaction. With scale-up to the 5-liter reactor, a 55 gallon drum was adapted with baffles to absorb the thermal and kinetic shock of the discharge. In this case, flashing to atmospheric pressure was sufficient to quench the reaction, thus dilution of the product with ice was eliminated.

Experimental Method

A typical procedure was as follows: the waste cellulose slurry at about 10% solids was poured into the autoclave, a typical charge being 1000 gm for the 1-liter reactor and 3000 gm for the 5-liter reactor. The autoclave was then electrically heated with stirring to various reaction temperatures, with 220-240 C found most desirable for optimum glucose conversions. The pressures required to obtain these temperatures were in excess of 500 psi. When the cellulose slurry reached the desired temperature, a predetermined quantity of acid was injected into the autoclave. This was accomplished using the inert gas from the nitrogen cylinder as the pressure medium to force the acid into the autoclave. The acid hydrolysis reaction was then run with continuing autoclave agitation for predetermined reaction periods, ranging from 5 seconds to more than 2 minutes. After reaction, the "quick release" ball valve was opened and the contents of the reactor were discharged rapidly so as to minimize hydrolytic degradation reactions of the glucose formed. The reaction mass was filtered to separate the glucose in the liquor for subsequent analysis.

Experimental Results

Two waste cellulose feedstocks were employed for the initial acid hydrolysis experiments, namely Wiley milled (75% greater than 50 mesh) and hydropulped Garden State Paper Company newsprint. The purpose of using the Wiley milled paper was to develop glucose conversion data which could be employed as a standard for comparison with the cheaper hydropulped feedstock. Hydropulping yields a much less finely divided and considerably less costly product than the Wiley milled material (estimated cost of hydropulping 1.65¢/lb, 5000 ton/day dry basis versus more than 6¢/lb for mechanically milled waste feedstock). If, therefore, comparable glucose values can be obtained, the basis exists for the development of a commercial process which is both technically and economically most attractive. This is particularly the case when it is considered that other pretreatment, such as UV exposure, chemicals, etc., may be employed together with the hydropulping to further enhance the yield of glucose.

Specific experimental data of typical acid hydrolysis runs which were carried out at 232 C in the autoclave setup as described earlier, are summarized in Figures 6-17. The data shows the glucose yields as a function of reaction time for a range of acid strengths, e.g. 0.58% to 2.24% (Figures 6-12). The 232 C temperature was employed for all the hydrolysis experiments run in this series because the results of previous experimental work had shown it to be optimal for glucose yield. The majority of the acid hydrolysis experiments were carried out with Wiley milled newspapers as the waste cellulosic feedstock in order to ascertain maximum glucose yields with an "accessible" feed as a function of acid content at 232 C hydrolysis temperature.

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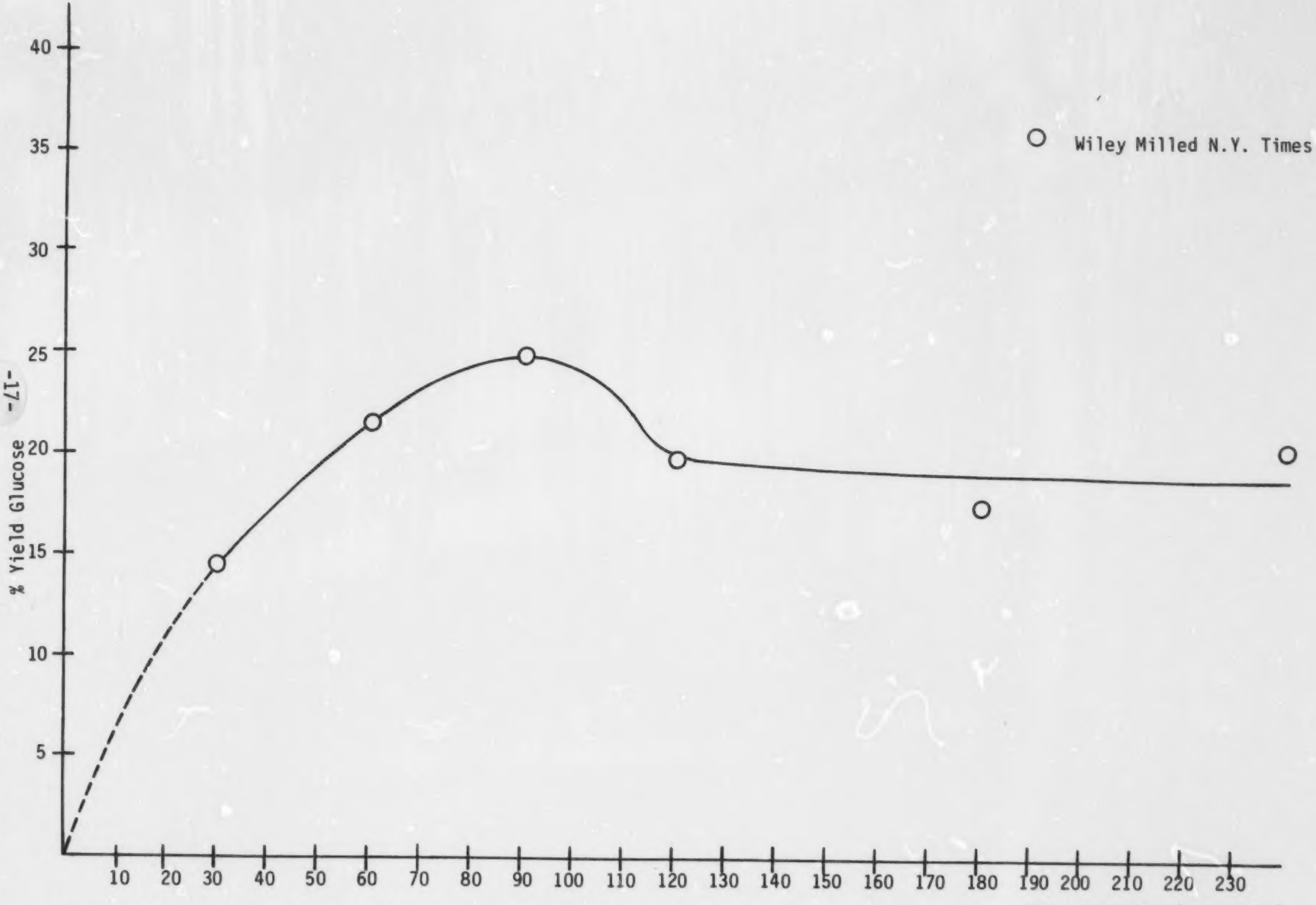

Figure 6. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 0.28% sulfuric acid and 450 F (232 C).

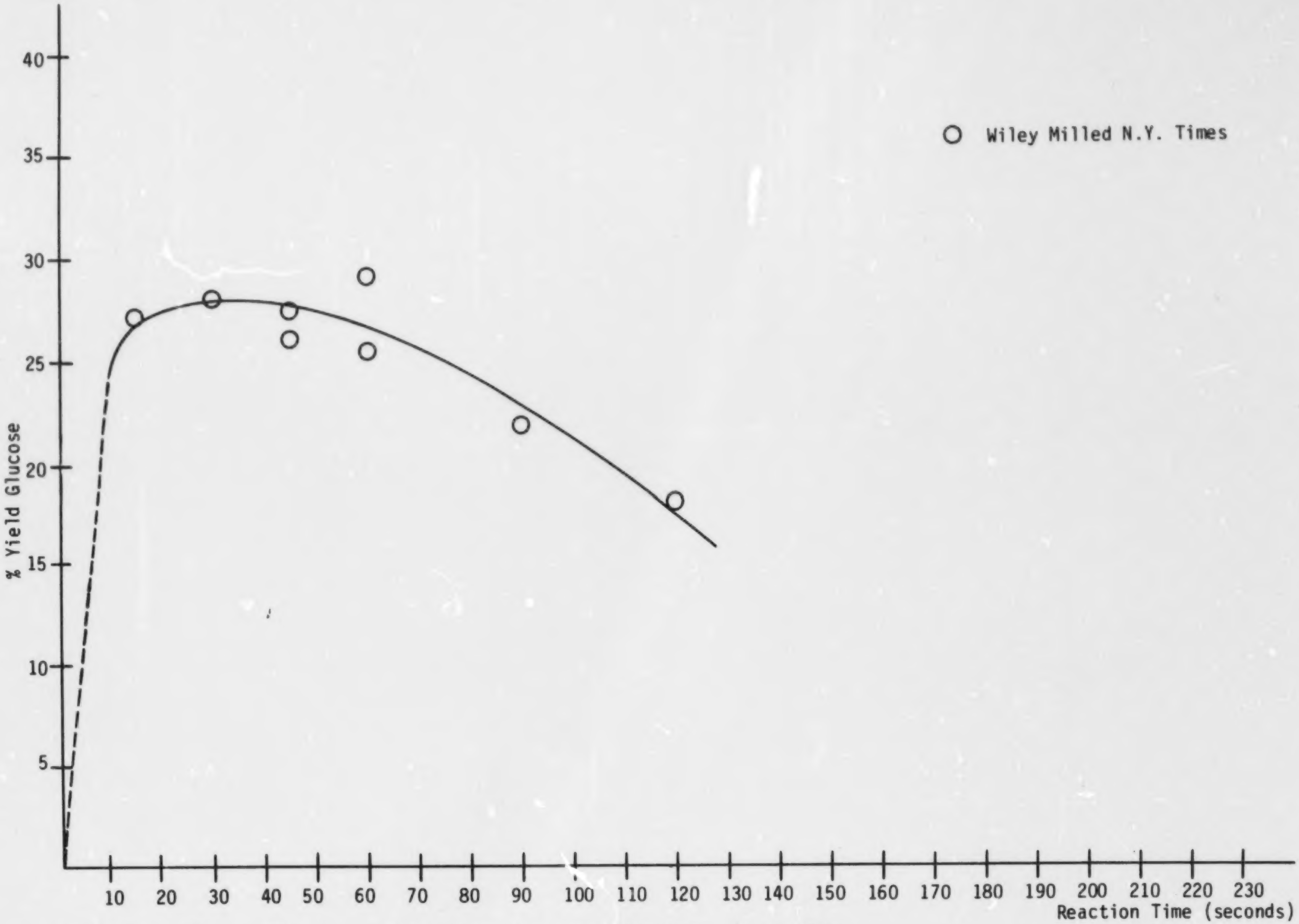

Figure 7. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 0.58% sulfuric acid and 450 F (232 C).

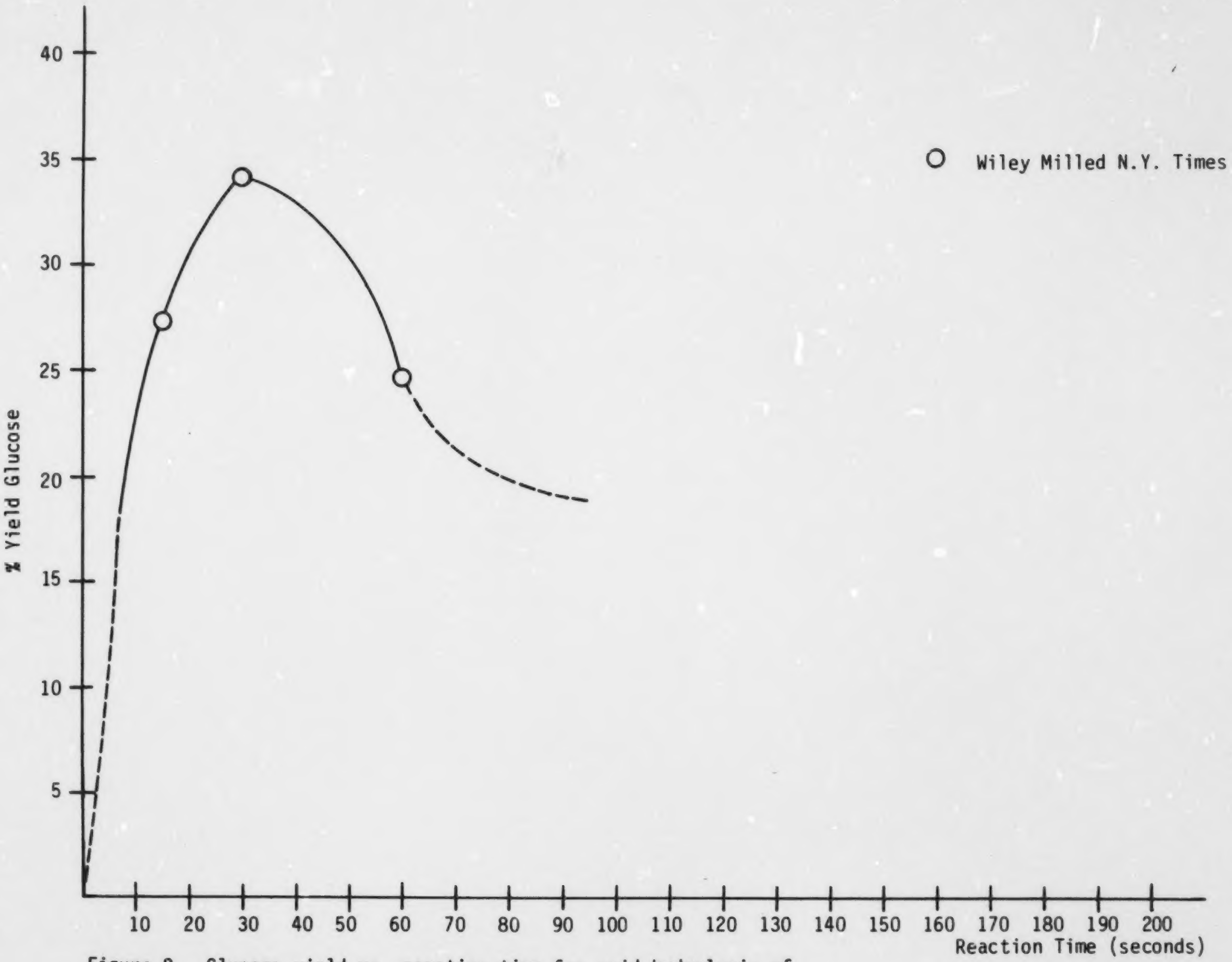

Figure 8. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 0.656% sulfuric acid and 450 F (232 C).

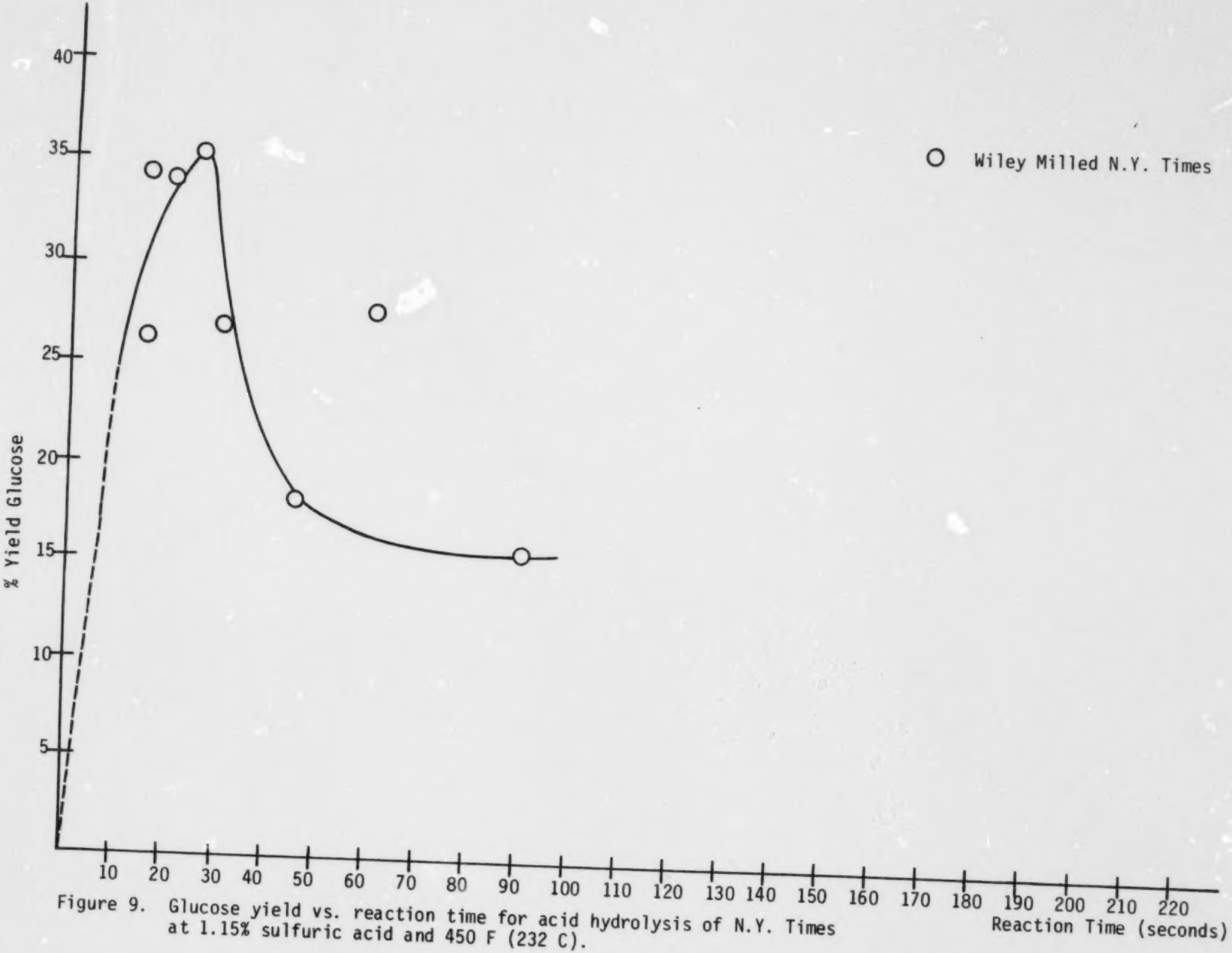

Figure 9. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 1.15% sulfuric acid and 450 F (232 C).

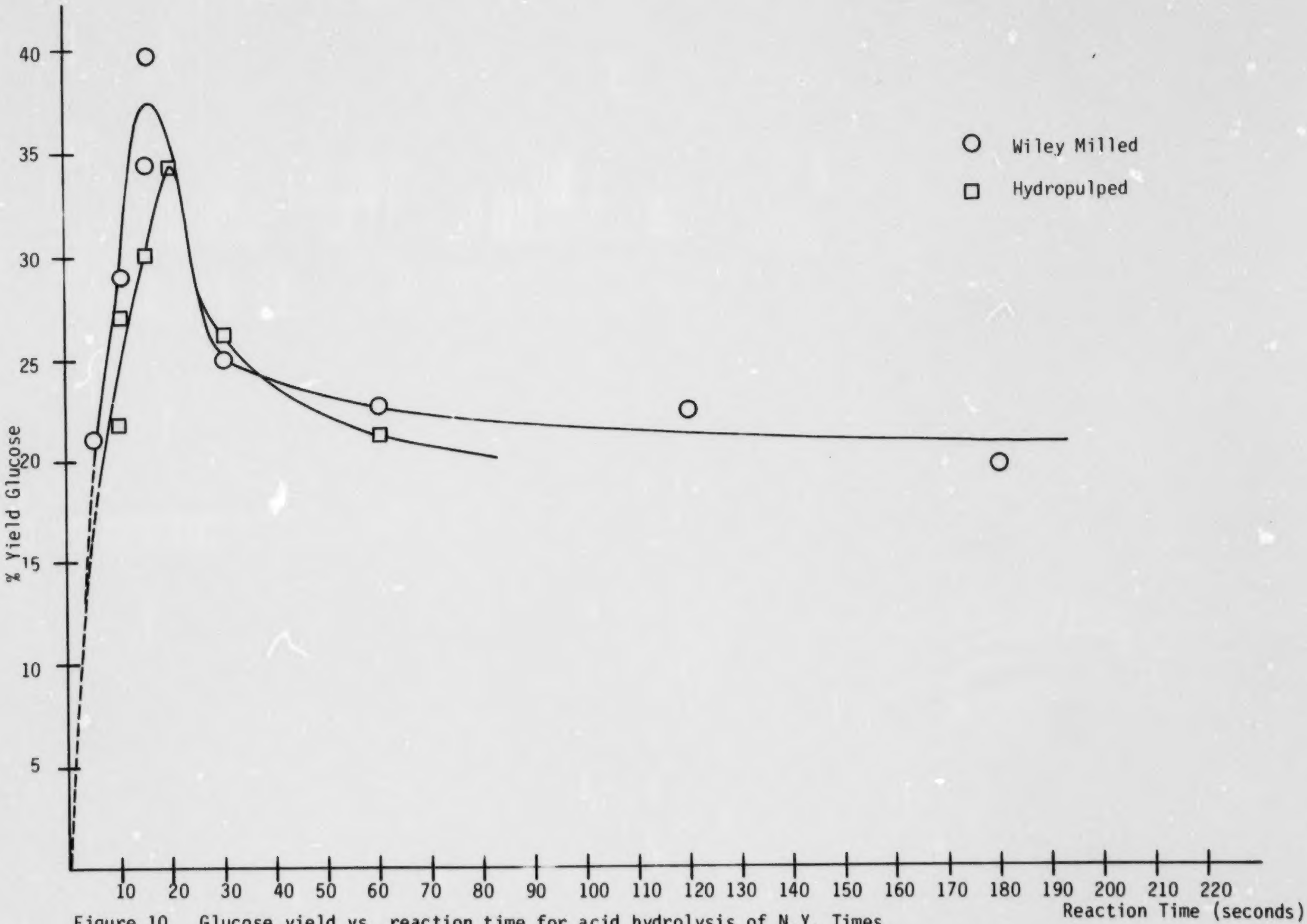

Figure 10. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 1.29% sulfuric acid and 450 F (232 C).

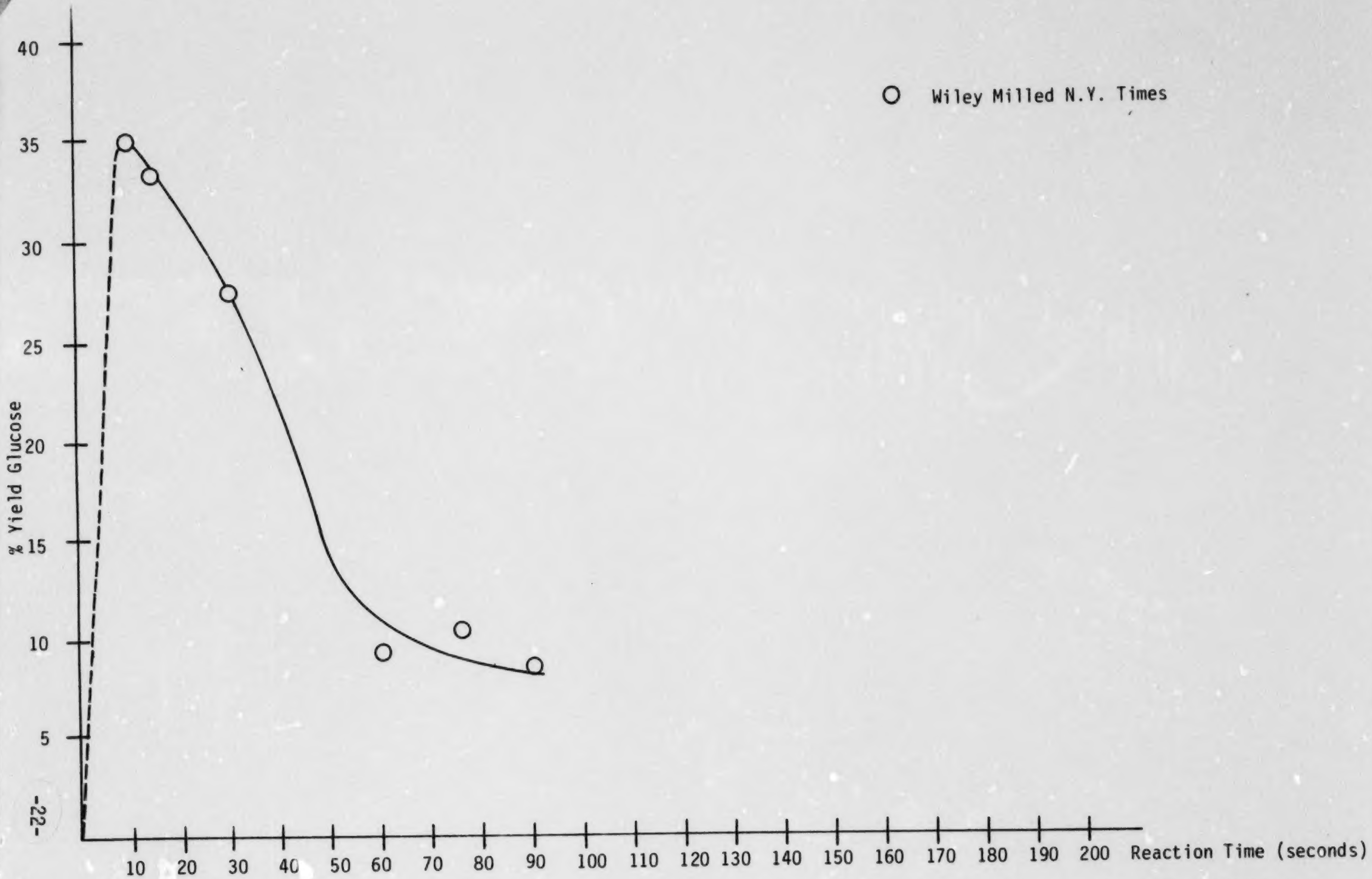

Figure 11. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 1.70% sulfuric acid and 450 F (232 C).

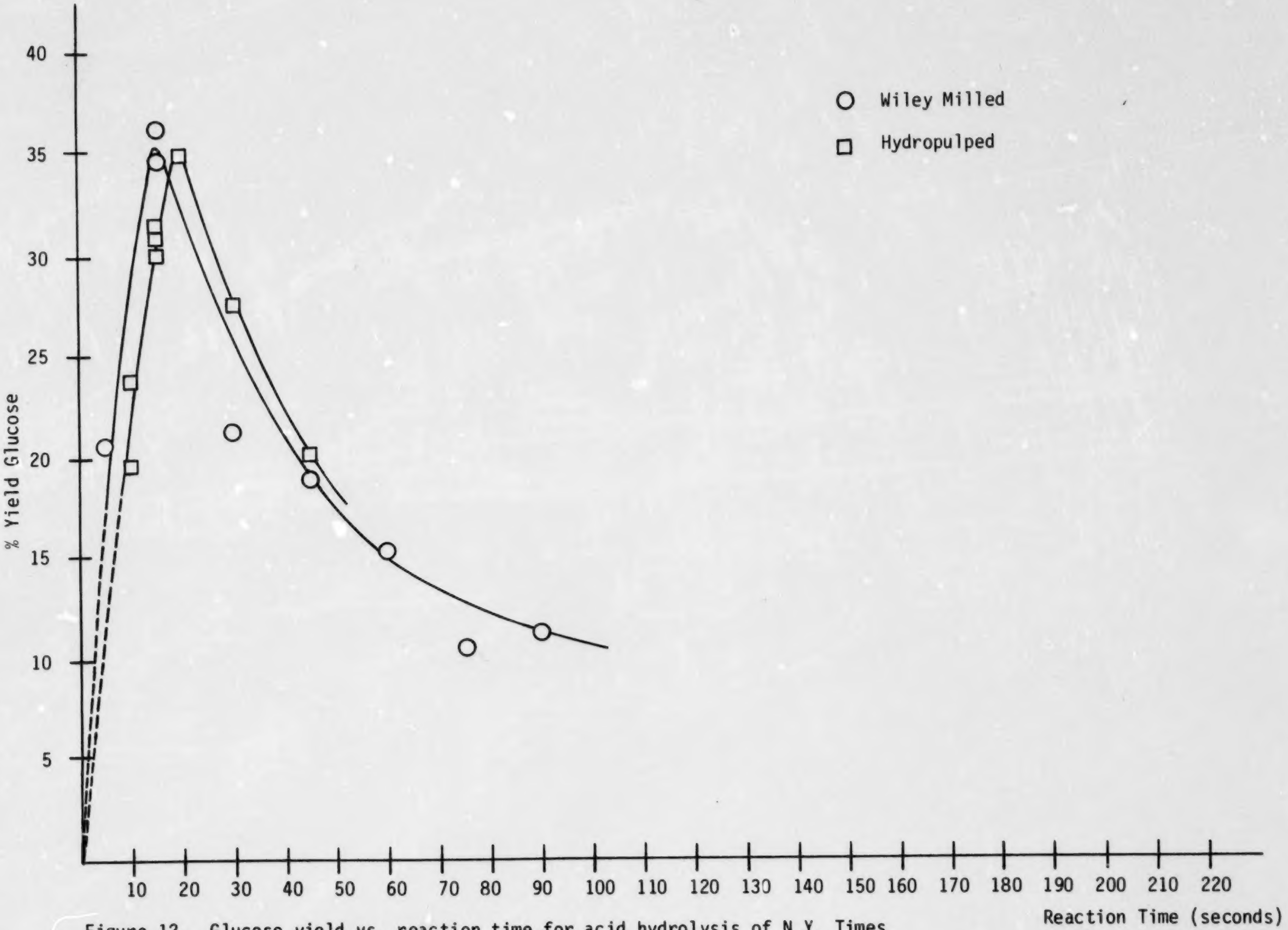

Figure 12. Glucose yield vs. reaction time for acid hydrolysis of N.Y. Times at 2.24% sulfuric acid and 450 F (232 C).

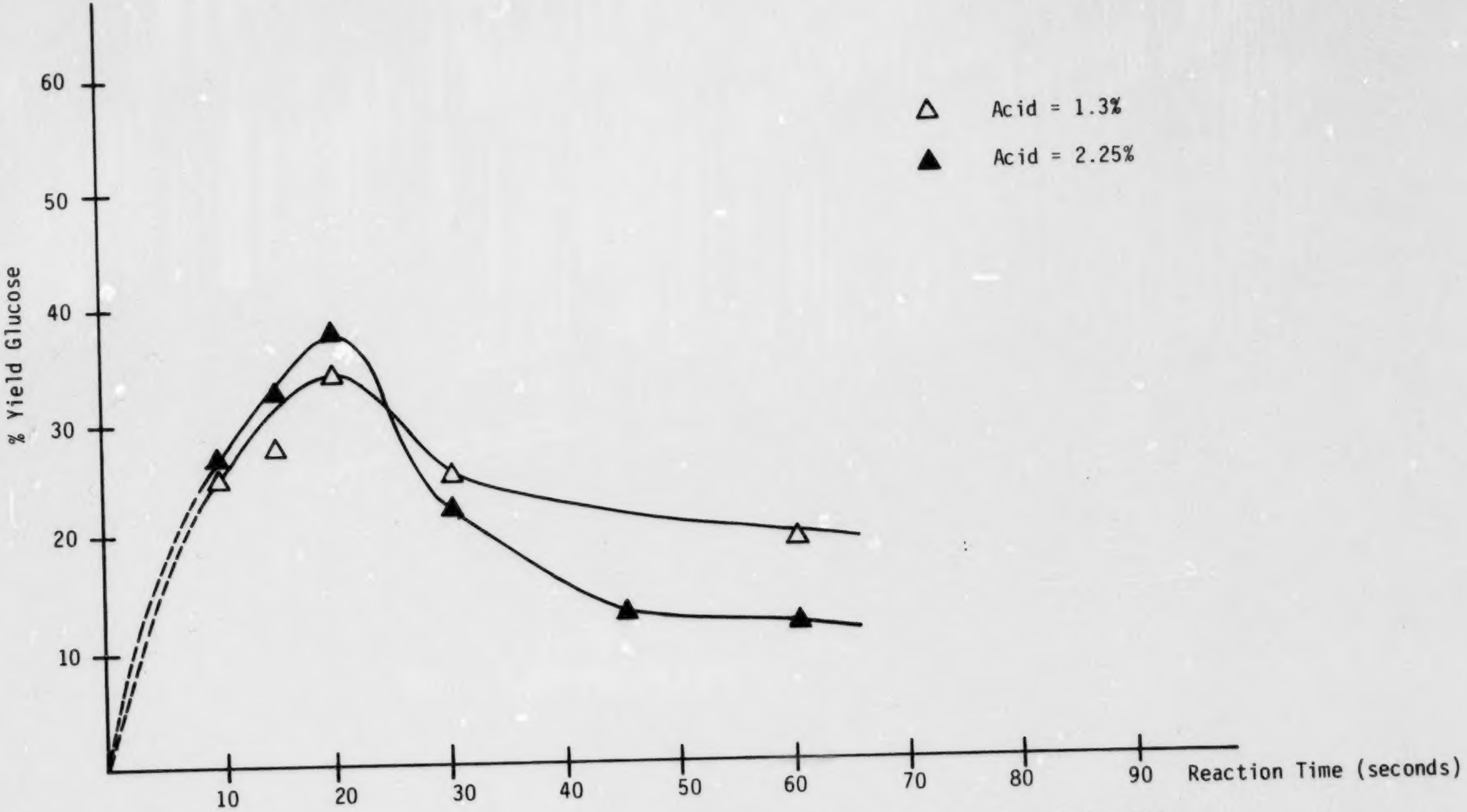

Figure 13. Glucose yield vs. reaction time for acid hydrolysis of hydropulped Garden State paper at 450 F (232 C).

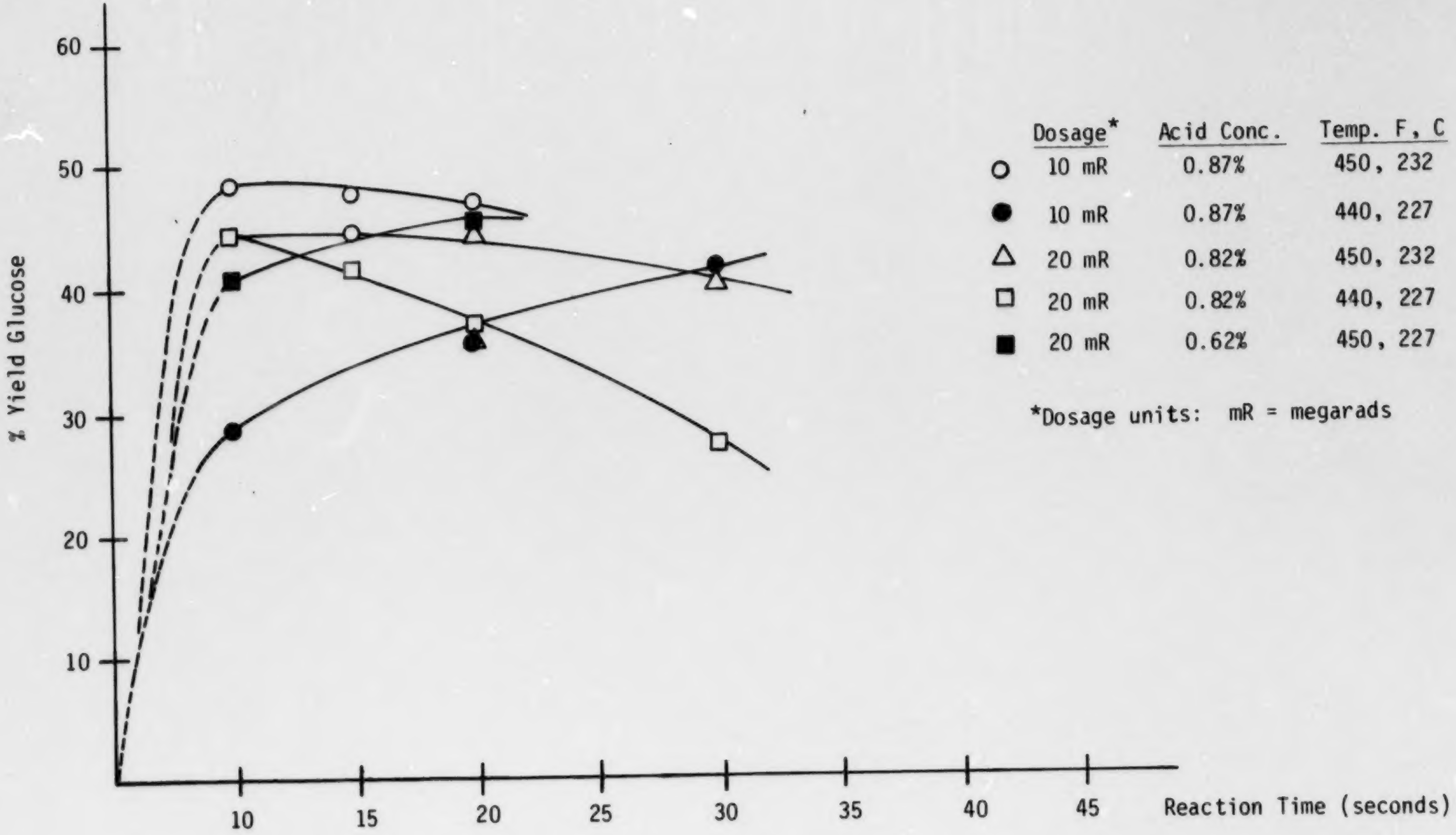

Figure 14. Glucose yield vs. reaction time for acid hydrolysis of Garden State paper; hydropulped and irradiated at two dosages.

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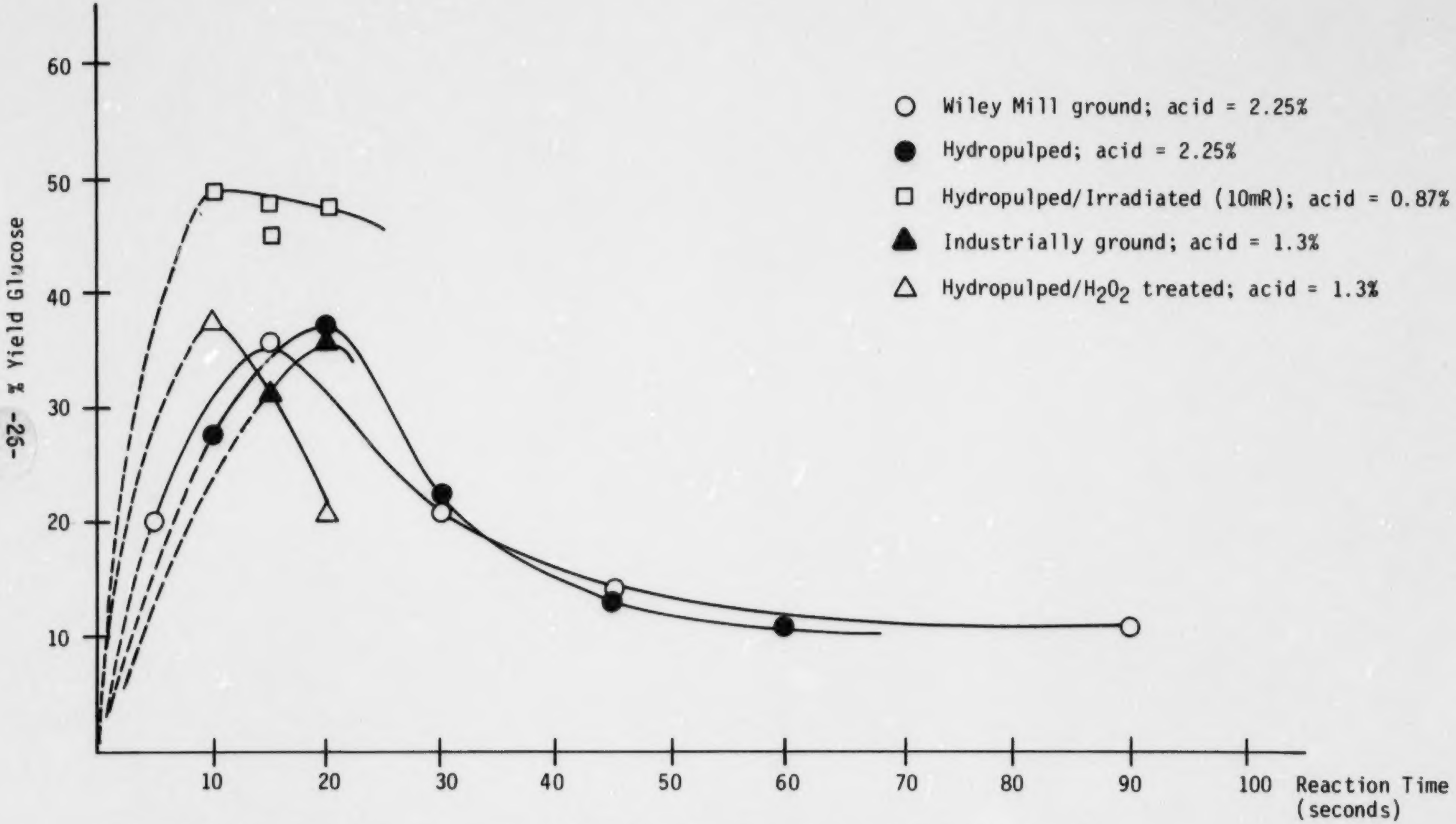

Figure 15. Glucose yield vs. reaction time for acid hydrolysis of Garden State paper at 232 C (450 F) for various pretreatments.

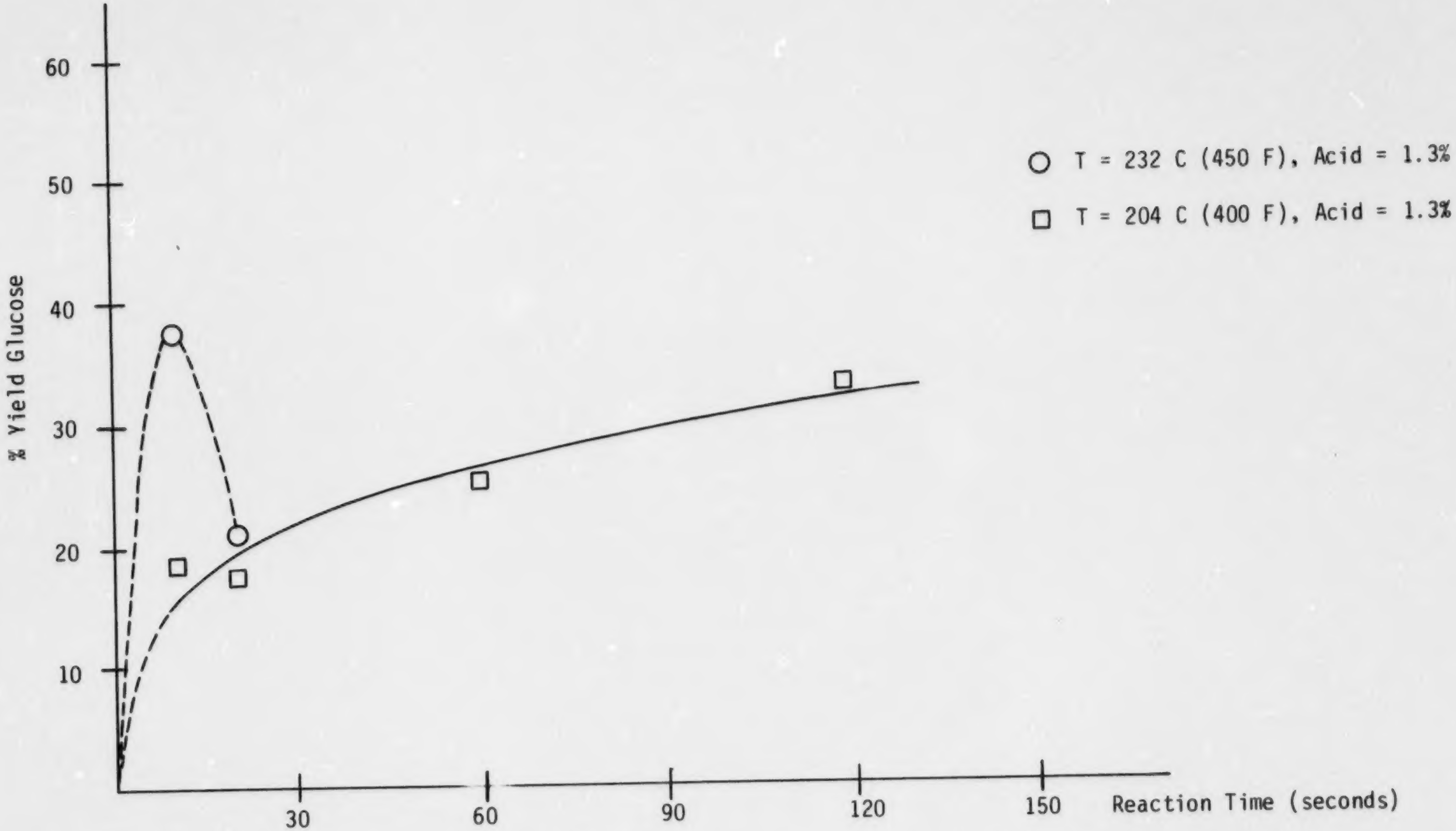

Figure 16. Glucose yield vs. reaction time for acid hydrolysis of hydrogen peroxide pretreated hydropulped Garden State paper.

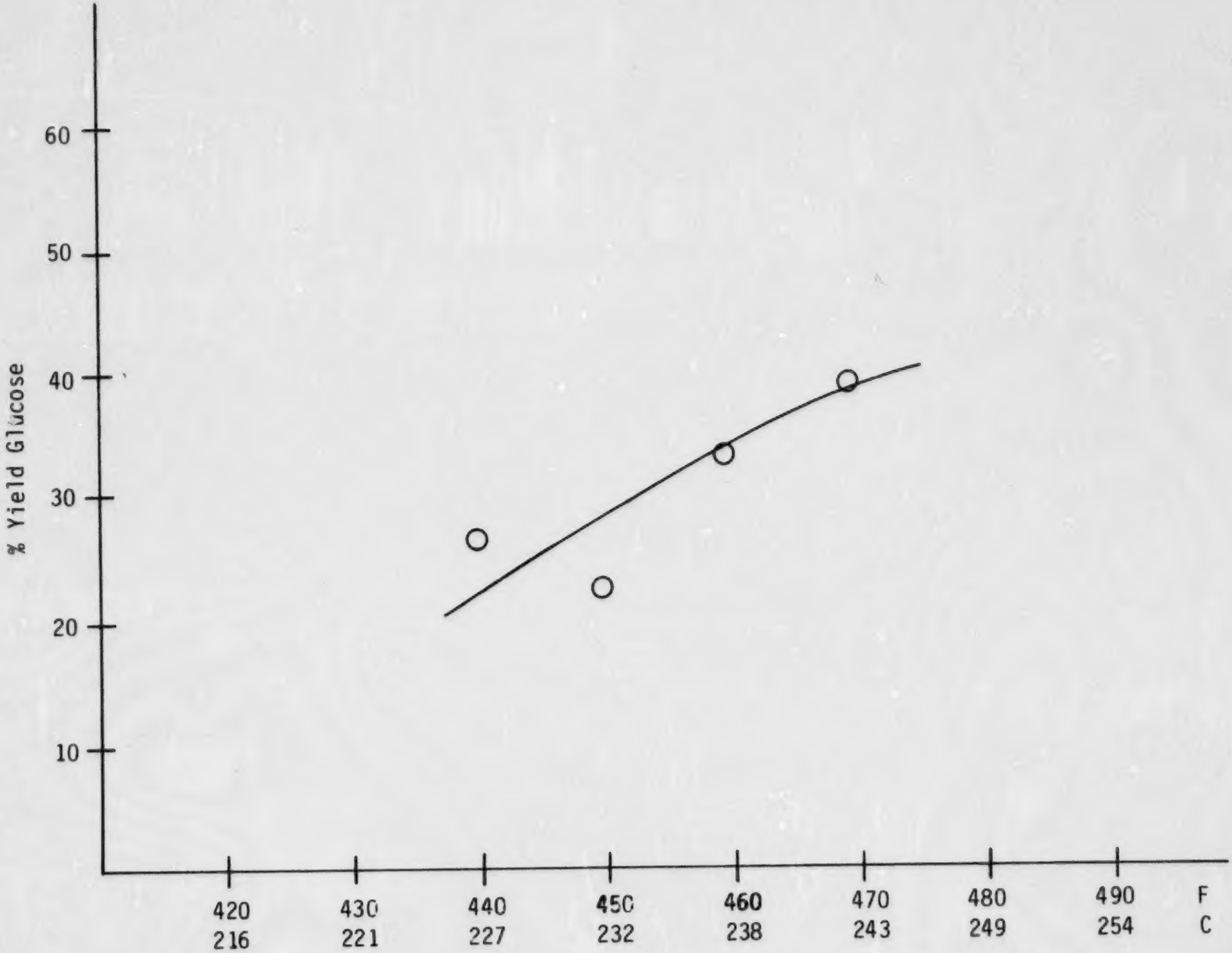

Figure 17. Glucose yield vs. reaction temperature for acid hydrolysis of hydrogen peroxide pretreated hydropulped Garden State paper. Acid = 0.87%. Residence time = 10 sec.

These experiments established the range of acid content which gave the highest glucose yields and the reaction times necessary to achieve them. Experiments with hydropulped cellulose feedstock were then run at three acid concentrations, 0.87%, 1.29% and 2.24%. The data for typical runs with hydropulped waste cellulose feedstock are shown in Figures 13-17. Glucose yields realized with this feedstock are indeed seen to be comparable with those obtained from Wiley milled material.

Conclusions

1) Maximum glucose yields increase with acid content while the reaction times necessary to achieve them decrease; the experiments carried out to date show that glucose yields on the order of 35% and higher can be obtained with acid strengths in the range of 1.30% to 2.25%, and reaction times for maximum glucose yields are 20 seconds or less at the preferred range of acid concentrations.

2) Hydropulped waste newspapers give glucose yields which approach rather closely those obtained from the more expensive Wiley milled paper; also, reaction times are similar. Thus glucose conversions on the order of 35% can be obtained in less than 20 seconds at the preferred range of acid concentrations, with cellulose concentrations in the slurries of 10%.

The following additional comments are in order on the specific autoclave hydrolysis technology being developed here which differs sharply from previous practices in this field.

1) *Minimal glucose degradation* as cellulose feedstock is only acidified after having been raised to the hydrolysis temperature, in contrast to previous practices where acidified cellulose solutions are heated to the hydrolysis temperature. This new procedure assures that the acidified cellulose slurry is exposed to the hydrolysis temperature for the minimum time period required for conversion to glucose, so losses of glucose during heating up are minimized. Also, the quick discharge valve on the reactor assures prompt removal of the reaction products and a *very* effective drastic decrease of their temperature, minimizing degradation during the cooling stage.

2) *Excellent mixing* throughout the critical acid hydrolysis reaction period; mixing quality is enhanced by the pressure injection technique of the acid.

3) *Equipment corrosion problems are minimized* because the acid used for hydrolysis is injected only when the waste cellulose slurry has attained the desired hydrolysis temperature and is only present at that temperature during the remarkably short reaction periods (20 seconds), followed by prompt discharge; thus, the entire hydrolysis system does not have to withstand dilute acid slurries of cellulose during heating up to the hydrolysis temperature. This is most important because dilute sulfuric acid is highly corrosive and presents many operational difficulties.

4) *Simplicity of operation and amenability to large scale production* employing either pressurized hot water or pressurized steam which can be used

to contact the waste cellulose to form hot slurries, etc., in a continuous process.

5) *Higher yields and short reaction times* can be translated into high throughputs with small equipment volumes; thus equipment investment requirements can be minimized with these short cycle times, which enhances the commercial attractiveness of this process.

6) *Use of pretreatments* such as UV, EB, chemicals, etc., combined with the above described hydrolysis procedure can help to further increase glucose yields.

B. CONTINUOUS HYDROLYSIS

Advantages of a Continuous Process

Once it was shown that the rapid dilute acid hydrolysis concept could be scaled up from Grethlein's capillary-type laboratory set-up (43) through the NYU 1-liter and 5-liter batch reactors, serious consideration was given to devising a method for making the process continuous, and scaling up further to a pilot plant, and ultimately industrial scale. Requirements are that a reaction vessel must be charged with feedstock and brought to the conditions of temperature, pressure, and acid content, then discharged within the few seconds required for optimum conversion. This would be impossible for a batch operation on an industrial scale, so if such a continuous process could be devised, it would overcome this short residence time difficulty as well as giving all the usual advantages of continuous over batch operations.

Equipment Selection

Clearly, any Lurgi-type arrangement would be inadequate, and the concept chosen was to employ a screw extruder as used in the plastics and candy industries as a reaction vessel. After a survey of available equipment, the machine selected for detailed testing was a co-rotating twin-screw extruder, Model ZDS-K53 by Werner & Pfleiderer Corp. (WPC) of Ramsey, NJ; 53 mm is the screw diameter, while the total screw length is about 3 meters. Figure 3 shows this machine as it was eventually set up.

Trials were carried out by WPC, NYU, and EPA personnel in the WPC commercial testing labs, then at Waldwick, NJ. Relevant parts of the test report are given in Appendix A.

One ton of Garden State Paper Company recycled newspaper pulp (8% solids) was fed to the extruder, heated, and discharged after acid was injected. Some difficulties were experienced in maintaining a steady feed rate with the mechanical dewatering of the slurry; it should be noted that fibrous cellulosic materials are generally known to be difficult to handle. Heating was solely electric, which limits the possible throughput, and no pressure seal was achieved at the discharge end, so no actual conversion to glucose was obtained. However, these trials showed that the extruder was capable of continuously conveying the cellulose slurry, bringing it up to the

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desired reaction temperatures, and injecting acid where desired. Throughputs on the order of 100 lb/hr were achieved.

The results were sufficiently encouraging to justify further investigation with this equipment, so arrangements were made to set up a pilot plant of capacity one ton (dry basis) feedstock per day at the NYU Labs at Westbury, Long Island, New York.

The Problems of a High Pressure Flow Reactor

Having established the feasibility of an extruder as a reaction vessel, many aspects of its operation still needed to be brought into practice. These included such things as the exact method for feeding while maintaining a pressure seal, the method for holding pressure at the discharge end, the accurate introduction of acid and steam, and so on. Thus, the main thrust of the NYU effort has been in "engineering" developments related to adaptation of the commercial extruder, as discussed in the remainder of this section; it is to be noted that the nature of this adaptation process is that it does not produce voluminous data -- a week's work, encompassing a significant advance, may result in no more than a single line of a report.

Most of the following discussion is separated into particular aspects of the process, rather than being a chronological record of experiments. As experience was gained with the equipment, it was soon evident that very accurate control of feed rates, moisture contents, steam and acid concentrations, etc., would be required to achieve our goals. The experiments conducted were for two distinctly different materials, a paper pulp of about 10% solids content and dry sawdust with a solids level of about 95%. Results in terms of conversion efficiencies (cellulose to glucose) are given at the end of the section.

Feedstock Handling

With a throughput of some one ton per day, the pilot plant extruder requires more than hand-feeding, and thus a materials-handling method must be developed for each feedstock of interest. It is anticipated that these methods can be scaled up for a commercial plant along conventional lines without significant difficulties.

For moving a waste pump slurry at around 10% solids content, which has the consistency of a pulp, the first approach tried was a Moyno pump. This is a "progressive cavity" type pump designed for slurries. Unfortunately, it proved able to handle the pulp only at solids contents below 7%. This is presumably due to the nature of the cellulosic feedstock, being firstly fibrous, and secondly having the characteristic of losing water in an irreversible manner when compressed; thus it very easily jams in pipes and machinery. In this connection, some slurries were first diluted, then subjected to dewatering tests in the extruder, to see if they could be handled in this way using the Moyno pump. It was soon decided that the idea was not worth pursuing, especially in view of the economic penalty of heating extra water, and use of the Moyno pump was abandoned. Subsequent handling was done manually; for a commercial plant, it is proposed to use conveyor belts for moving paper pulp.

For handling dry feedstocks such as sawdust, with a higher volume throughput, an agricultural auger-feeder was purchased and adapted, and proved quite adequate.

Feeding

Initial trials at the WPC facility revealed that gravity feeding would be inadequate for paper pulp, so a crammer feeder was incorporated in the design for NYU (see Figure 18). This consists of a conical hopper above a smaller conical feeding tube, with a variable-speed motor to drive a single vertical shaft bearing agitator bars in the hopper and a screw in the feeding section. A jacket is provided through which a heating fluid may be circulated, and the whole device is constructed of 316 stainless steel and amounted firmly on the extruder. In operation, this indeed forced pulp into the extruder feed port at suitable rates.

Moving to dry feedstocks, the gearing ratio on the crammer was increased from 10:1 to 60:1 to give a higher feed rate. Later, however, the bottom section of the crammer was replaced by a transparent plexiglas tube arrangement, in order to facilitate cleaning up of the feed region in cases of "blow-back" of reaction material as described later; it was believed that gravity feeding would be adequate for dry feedstocks. One problem encountered was that of electrostatic effects in the tube, which was countered by grounded metallic inserts. Another problem was that of irregularities in the feed rate due to sawdust variability and bridging tendencies, which was countered firstly by installing a vibratory-tray type feeder (Eriez Magnetics "Hi-Vi" Model 20A) between the auger and the extruder. Secondly, this was combined with, and later replaced by, an Acrison volumetric feeder, which is designed to handle materials that tend to bridge. It employs inside a hopper an agitator in the form of a large horizontal helical screw with both left- and right-handed sections, and a smaller concentric feeder screw, also helical, which conveys the material through a feeder tube to be dropped into the next processing stage (here the vertical tube leading to the extruder feed-port). This arrangement is shown in Figure 19.

Dewatering

As a slurry-type raw material such as paper pulp is fed into the extruder, it passes through a section in which the screw elements compress as well as convey, so that water is forced from it and runs out a port in the bottom of the extruder barrel. This water carries with it a small proportion of the solids, and typically has a solids content of 1%, but the loss is not significant. After being dewatered in this manner, the paper pulp has a solids content of some 60%. Most dry feedstocks pass through this section without change, but some, such as "green" sawdusts of high moisture content, similarly lose a part of their moisture through the dewatering port.

Dynamic Plug: Formation and Stability

An account of the operating principle of the plug is given in the

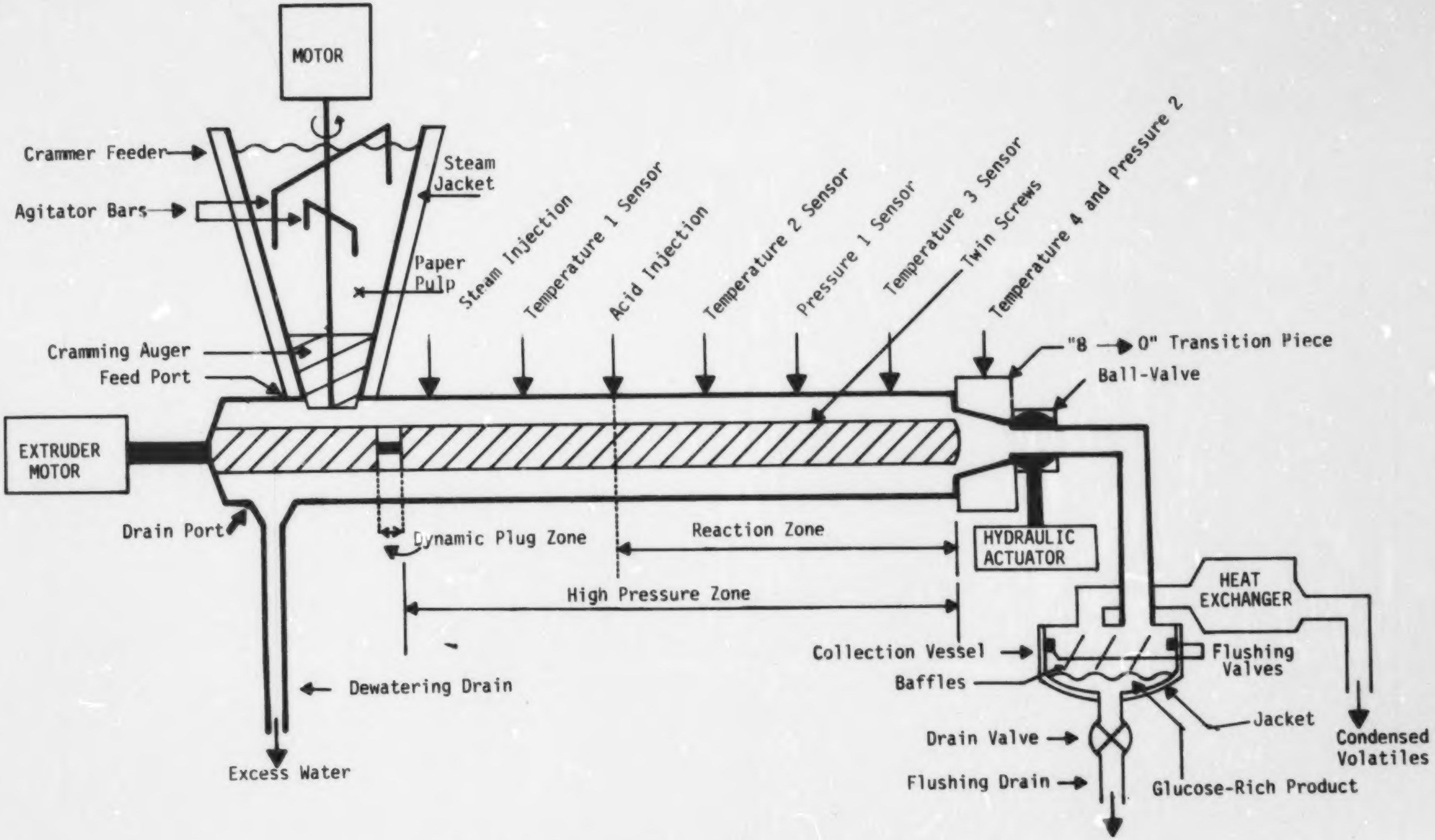
MOTOR
Crammer Feeder
Agitator Bars
Steam Jacket
Paper Pulp
Cramming Auger
Feed Port
EXTRUDER MOTOR
Drain Port
Steam Injection
Temperature 1 Sensor
Acid Injection
Temperature 2 Sensor
Pressure 1 Sensor
Temperature 3 Sensor
Twin Screws
Temperature 4 and Pressure 2
"8 → 0" Transition Piece
Ball-Valve
HYDRAULIC ACTUATOR
Dynamic Plug Zone
Reaction Zone
High Pressure Zone
Dewatering Drain
Excess Water
HEAT EXCHANGER
Collection Vessel
Baffles
Flushing Valves
Jacket
Condensed Volatiles
Drain Valve
Flushing Drain
Glucose-Rich Product

FIGURE 18: Schematic of the New York University Hydrolysis System: Arrangement for "Wet" Feedstocks

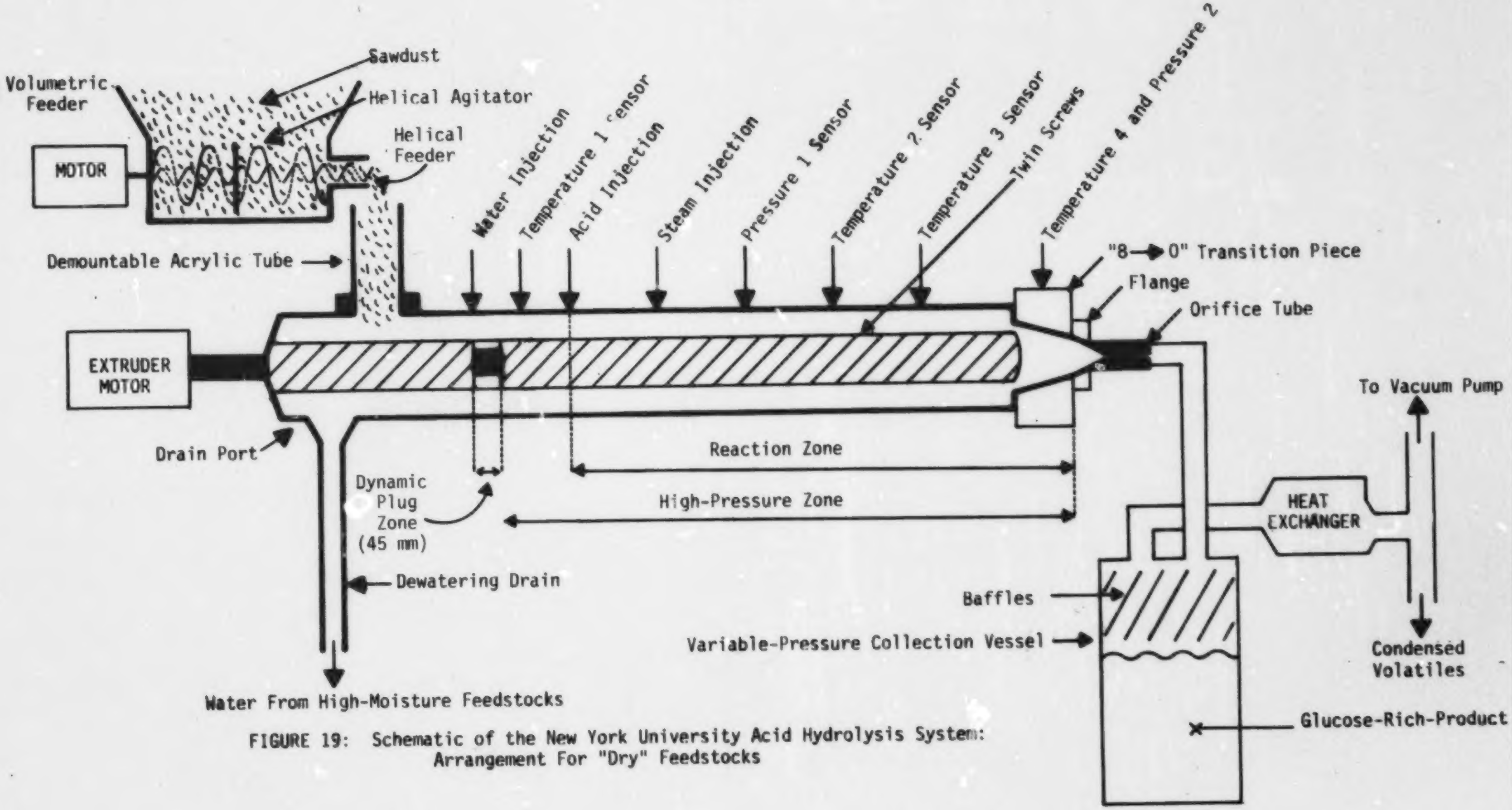
Sawdust
Volumetric Feeder
Helical Agitator
Helical Feeder
MOTOR
Demountable Acrylic Tube
Water Injection
Temperature 1 Sensor
Acid Injection
Steam Injection
Pressure 1 Sensor
Temperature 2 Sensor
Temperature 3 Sensor
Twin Screws
Temperature 4 and Pressure 2
"8→0" Transition Piece
Flange
Orifice Tube
EXTRUDER MOTOR
Drain Port
Reaction Zone
High-Pressure Zone
Dynamic Plug Zone (45 mm)
Dewatering Drain
Water From High-Moisture Feedstocks
To Vacuum Pump
HEAT EXCHANGER
Condensed Volatiles
Baffles
Variable-Pressure Collection Vessel
Glucose-Rich-Product

FIGURE 19: Schematic of the New York University Acid Hydrolysis System: Arrangement For "Dry" Feedstocks

Summary, Section 2 of this report. Although the operation cannot be directly seen, a plug may be examined at leisure by stopping a run and removing the twin screws from the extruder barrel; the plug is found to be densely compacted, resembling Masonite after cooling down and drying out. During operation, shear stresses in the plug zone comprise most of the torque demand on the extruder motor, and thus plug behavior may be monitored by following the torque supplied. Central to formation and control of the dynamic plug is the particular configuration chosen for the screw bushings, both within the plug zone and up- and downstream of it; a typical screw configuration is shown in Figure 20.

An individual bushing in this screw configuration diagram is specified by a designation such as "45/90 L.H." In this, "45" means that the screw pitch is such that one revolution corresponds to an axial conveying distance of 45 mm (assuming no slip); "0/90" would refer to a bushing with no conveying crests, or a "blank". The "90" is the length of the bushing in millimeters, and "L.H." stands for Left-Hand, i.e. reverse pitch. There are also available various other specialized types, such as "kneading block elements". A complete description would also include materials information such as 316 stainless steel or nitrided steel, whether wear-resistant crests have been welded on, and so forth.

Initially, a screw configuration suggested by WPC was used, having several left-hand elements a short distance downstream from the feed port to form the plug. A description follows of the major changes made to this configuration for various reasons, and should help to explain the practical aspects of operating with a dynamic plug.

Dropping the screw speed (from 300 to 120 RPM) in order to give a longer residence time, it was found that the plug became unreliable, so a "stronger" plug configuration was substituted, namely, a 0/180 blank and a 90/30 left-hand element. This turned out to be overkill, as the material was not conveyed past the plug, but was forced out the dewatering port; a demonstration of the great sensitivity of the dynamic plug. Removing the left-hand element allowed the material to pass, but the torque levels fluctuated up so high as to cause motor cutouts, thus the blank element length was reduced from 180 to 75 mm, and this proved to operate satisfactorily. However, attempting next to reduce the torque and thus the energy consumption by further shortening the plug (to an 0/45 blank) led to instability in holding pressure, so the 0/30 element was reinstalled to return to the 75 mm plug.

It was also discovered that any heating in the plug zone gave rise to erratic behavior. This was presumed to be due to partial drying of the material, causing variations in the shearing stresses, so the barrel heaters in this zone were afterwards routinely left off.

On changing from paper pulp to the dry feedstock sawdust, it was immediately found that behavior of the dynamic plug was different from that with the pulp. Although the crammer gearing had been changed to give a higher volumetric feed rate, the plug formed was much less stable: there was a tendency for it to fail suddenly, leading to a blowback of reaction material through the feed port. Unfortunately, even slight amounts of steam creeping

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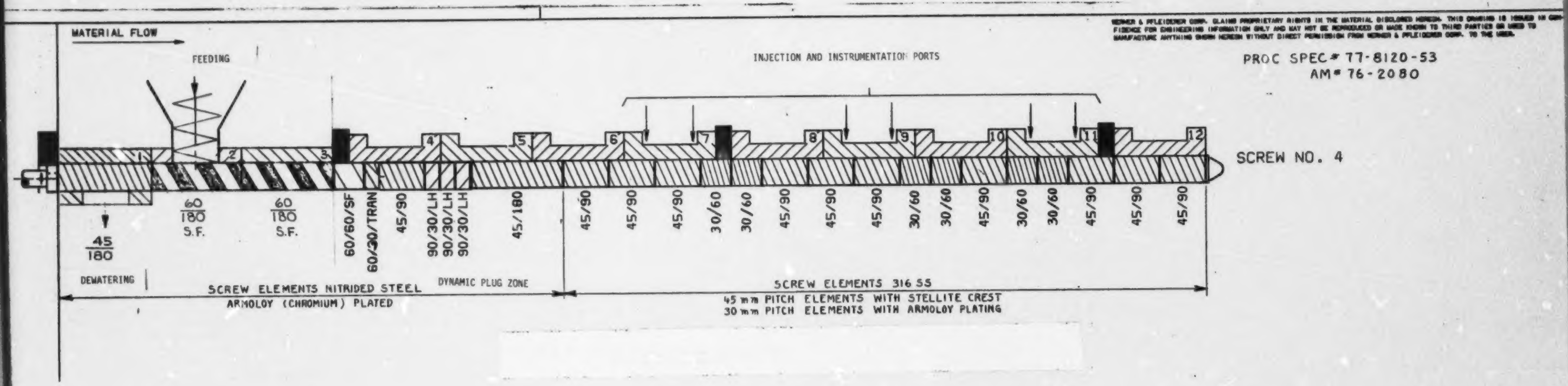
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MATERIAL FLOW
FEEDING
INJECTION AND INSTRUMENTATION PORTS
1
2
3
4
5
6
7
8
9
10
11
12
SCREW NO. 4
45/180
60/180 S.F.
60/180 S.F.
60/60/SF
60/30/TRAN
45/90
90/30/LH
90/30/LH
90/30/LH
45/180
45/90
45/90
45/90
30/60
30/60
45/90
45/90
45/90
30/60
30/60
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30/60
30/60
45/90
45/90
45/90
DEWATERING
SCREW ELEMENTS NITRIDED STEEL
ARMOLOY (CHROMIUM) PLATED
DYNAMIC PLUG ZONE
SCREW ELEMENTS 316 SS
45 mm PITCH ELEMENTS WITH STELLITE CREST
30 mm PITCH ELEMENTS WITH ARMOLOY PLATING

FIGURE 20: Typical Extruder Screw Configuration (With permission of WPC)

back from the plug through the feed port to the crammer caused the sawdust to become damp and to feed unevenly, thereby aggravating the plug instability. In each case, when the run was stopped, there remained wet sawdust filling the feeding and hopper parts of the crammer; this then had to be removed and the crammer auger, etc., completely dried before any more sawdust could be fed into it. By removing the lower part of the crammer feeder and replacing it with a simple transparent plexiglas tube arrangement attached to the extruder feed port, the clean-up work was greatly reduced, and it became possible to watch any feed problems as they developed.

Several methods were tried for improving the plug stability. First, the length of the blank bushing section was increased, just as described for the case of paper pulp, from 60 to 90 mm; an improvement was noted, but results were still unsatisfactory. Attempting then to pack more sawdust into the plug by changing to screw configurations with high-pitch elements upstream led to feeding at too high a rate, and thus to high-torque cut-outs of the extruder motor; this was countered by shortening the plug zone again, from 90 mm to 45 mm.

A screw configuration was devised so as to form a double dynamic plug at the feed end, in the hope that any brief loss of integrity of one plug would be covered by the other, so that no significant amount of blowback would occur; in practice, this arrangement proved difficult to operate, any gain in plug integrity being outweighed by stoppages due to excessive torque fluctuations. On returning to a single plug, some high pitch elements were again inserted immediately before it, in order to pack material into it more rapidly.

Following up the observation mentioned for pulp, that heating around the plug zone led to instability, efforts were made to increase the moisture in the plug. Firstly, the acid injection point was moved to a port further upstream, from Port 3 to Port 1, close to the plug. Later, it was moved downstream again, but the results appeared inconclusive. Presumably this was due to the essentially downstream movement of liquids inside the extruder barrel, so that none of the acid could directly make its way upstream to the plug zone: only the steam can do this, and that of course is part of the problem. Secondly, the acid injection rate was increased (from 77 to 102 lb/hr), giving a moisture content in the reacting mixture of 50%. Again, results were essentially inconclusive with respect to plug stability, presumably for the same reason as stated above.

However, by far the most significant step towards stabilizing the plug was the direct injection of water just before it, in order to ensure that it had appropriate moisture content. This was done initially by drilling a new hole in the extruder barrel, called "Port 0", and using another pump to feed water into it. Running the reactor in this mode, plugs of satisfactory integrity were obtained. To verify the stability effect, a capability was added to divert the water injected during a run to the acid injection point (Point 3), thus keeping other variables constant; indeed, a reversion to less stable operation sooner or later ensued. Steady operation was attained routinely by this water injection method, runs being stopped voluntarily after periods as long as 75 minutes.

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Discharge Methods

Initially it was hoped that a seal could be maintained at the discharge end of the extruder in the same manner as at the feed end, namely by forming a dynamic plug. Throughput trials of paper pulp using a screw configuration with left-hand bushings (90/30) led to some transient plugs; tests were then made injecting acid as well, but no hydrolysis of the cellulose was observed. In order to get a more positive method for holding pressure at the discharge end, it was decided to abandon, at least temporarily, the dynamic plug (i.e., remove the left-hand elements), especially since with hydrolysis the material would be less fibrous and correspondingly even less likely to form a satisfactory plug.

In its place would be a valve, the first choice being a ball valve as most likely to perform adequately under the conditions. A manually-actuated valve (Jamesbury Corp., Worcester, MA) was installed, and with 200 psi pressure in the reaction zone, some fiber breakdown was observed in the product as evidence of hydrolysis. However, the Teflon seat of the ball valve soon failed, and had to be replaced. On the next test, at 220 C and 300 psi, the first positive test was obtained for glucose.

Again the ball valve soon began to leak, but the concept had been demonstrated, so a more appropriate ball valve was ordered (Kamyr Valves Inc., Glens Falls, NY: 1½ inch Reduced Bore, Severe Service Type; hastelloy ball and stem, stellite seat, graphite packing, Model RNC-015-AAS-H). It was decided to actuate this valve hydraulically, so an appropriate rack-and-pinion gearing system and hydraulic circuit (see Figure 21) were designed and constructed by NYU personnel, although prior opinions received from experts in the field maintained that such a valve could not be cycled as quickly as specified.

Once the Kamyr valve, and its hydraulic actuating system, were connected, a suitable electro-mechanical timer was added and set to give it a cycle (see Figure 22) from normally closed, through a brief opening for discharge of hydrolyzed material, to closed again, over a period of several seconds (typically one 1/30 second discharge every 20 seconds, a complete sequence actually including the same cycle in reverse). The duration of the opening could be adjusted if necessary by choking down on the hydraulic oil between the solenoid valve and the piston with a pair of graduated flow-control valves (one for each direction of the rack gear). Now a run could be started up with the discharge end positively closed until the desired pressure and time were attained, and only then a carefully controlled discharge cycle could be added.

After a series of runs had been carried out using the hydraulic ball valve, and demonstrating the basic practicality of the extruder hydrolysis concept, some approaches were tried to a completely continuous discharge. To summarize briefly, (i) a heavy-duty ball-and-spring arrangement was constructed, functioning essentially as a pressure relief valve; in operation, this discharge was in fact only semi-continuous, with some re-seating difficulties, and the pressure was not maintained sufficiently steadily; (ii) a cone-and-spring construction was developed from the ball-and-spring just mentioned; it also failed to operate completely continuously; and (iii) a pair of ball

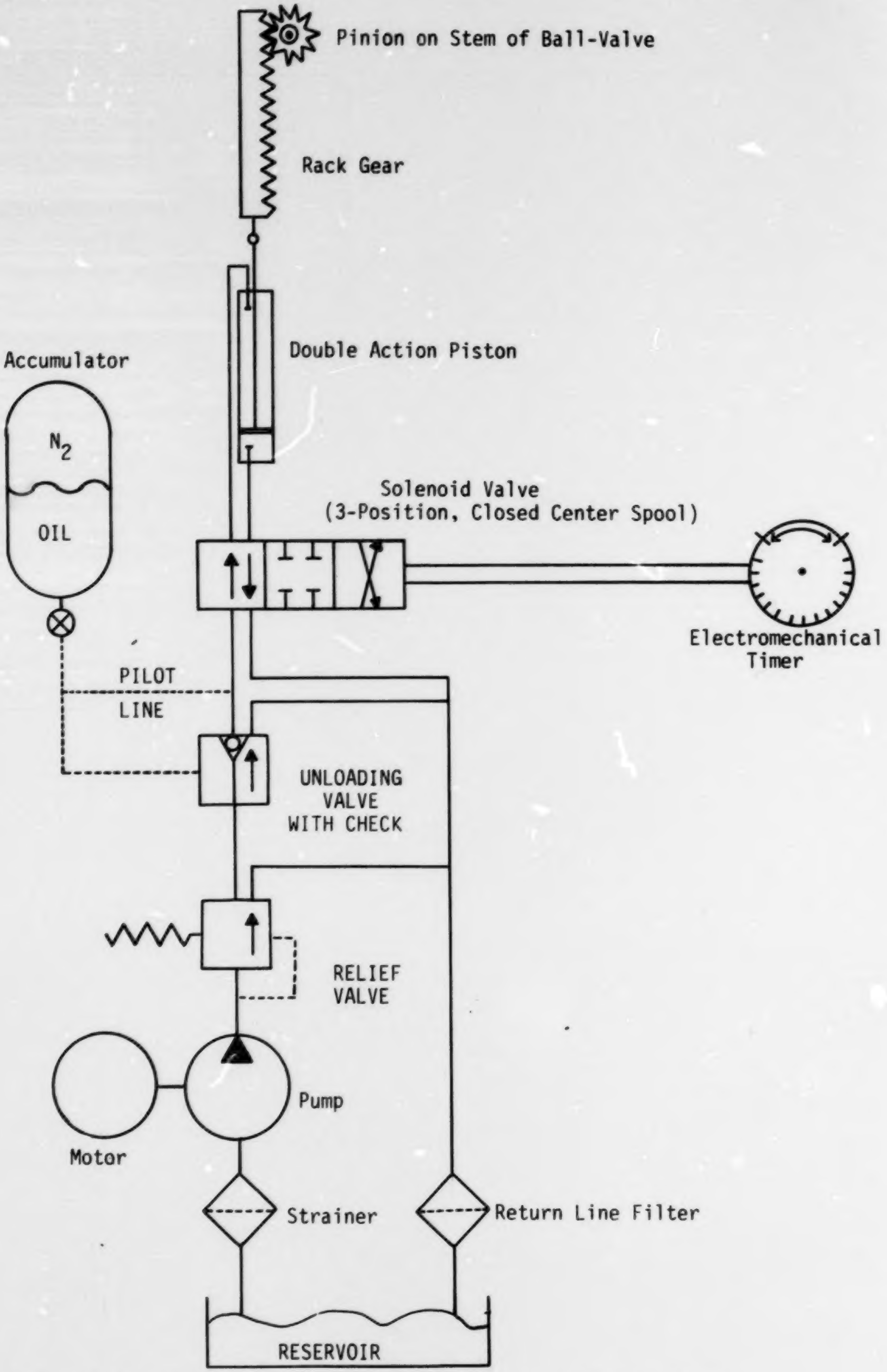
Pinion on Stem of Ball-Valve
Rack Gear
Double Action Piston
Accumulator
N_2
OIL
Solenoid Valve
(3-Position, Closed Center Spool)
Electromechanical
Timer
PILOT
LINE
UNLOADING
VALVE
WITH CHECK
RELIEF
VALVE
Motor
Pump
Strainer
Return Line Filter
RESERVOIR

FIGURE 21: Hydraulic Actuator System For Ball Valve Discharge

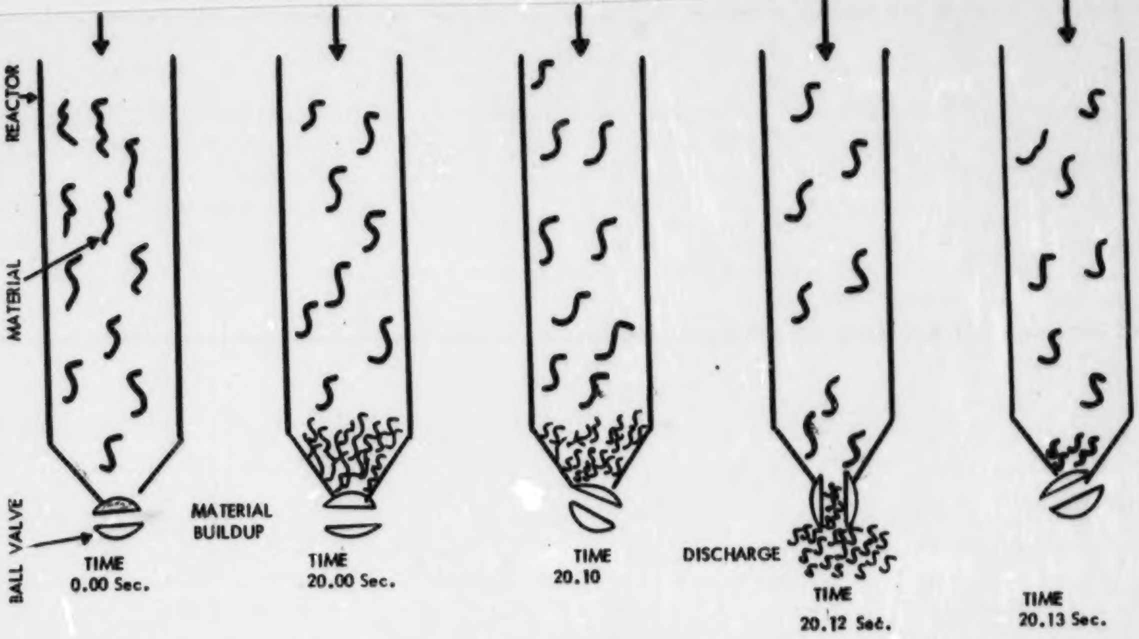
REACTOR
MATERIAL
BALL VALVE
TIME
0.00 Sec.
MATERIAL
BUILDUP
TIME
20.00 Sec.
TIME
20.10
DISCHARGE
TIME
20.12 Sec.
TIME
20.13 Sec.

Figure 22: Ball valve operation; material discharged, pressure retained.

valves were set up to operate out-of-phase, so that the drop from reaction pressure to atmospheric would occur in two steps, and hence the cycling could be more rapid, with the net result of a more even reaction pressure and better residence time distribution: it proved difficult, however, to keep the extruder pressure high enough for hydrolysis, and this approach was not considered immediately promising.

Ultimately, after the period of this EPA contract, a successful system was developed for truly continuous discharge using an orifice. This is now in regular operation, and a screen is provided to minimize blockages of the orifice. It is intended to add a capability to rapidly exchange screens during hydrolysis; this would require only modification of equipment supplied by WPC, and should prevent the occasional blockage of the screen, which appears to be the last remaining problem in continuous operation.

Collection

Considering the process of discharging the extruder contents from reaction conditions to ambient, it is clear that a considerable expansion will occur, and that a large flow of acidic product and steam must somehow be collected and treated. A cyclone was the first method tried, but it tended to form a plug leading to an explosion, and was abandoned. In its place was used simply a large plastic drum with a hole in the lid, held down by weights; this served the purpose, even with the almost explosive discharge sequence from the ball valve, until a more permanent and effective system was arranged.

As shown in Figure 18, the collection vessel used for a considerable period was based on an industrial jacketed stainless steel kettle; it was securely mounted to the floor, equipped with a drain and double-arm garden-type sprinkler for washing down, and the lid was pulled down onto a high-temperature rubber gasket by a set of quick-release butterfly nuts. A sampling port was added by cutting a hole in the kettle lid, welding the cut-off rim of a domestic pressure cooker into the hole, and then using this for quick access to the product. Thus, in between ball valve openings, a dexterous operator could twist off the pressure-cooker lid, dip out a sample, and replace the lid. In practice, another operator was stationed for safety to override the ball valve timer temporarily if there was any delay.

Figure 19 shows the currently-used collection system, which is based on a 55-gallon drum. A drum-liner, essentially a heavy-duty plastic bag, serves to hold the product for weighing and sampling, followed later by sealing and hoisting to a fiber carton for storage or fermentation. Baffles are fitted to the removable lid to aid in separating vapor from liquid and solid; the vapor is passed through a commercial shell-and-tube heat exchanger to condense the liquid components. In terms of the overall process, however, the significant difference from the kettle is the provision for variable pressure. A vacuum pump allows discharge to pressures down to 28" Hg, or 1 psia. Alternatively, the pressure inside the collection drum can be maintained above atmospheric, allowing discharge to intermediate temperature and pressure; Hajny (13) recommends discharge to 140 C for improved fermentability. One of the main advantages of this variable-pressure arrangement is to allow some choice of distribution of the volatile products, such as furfural, between the glucose fraction in the drum and the condensate fraction; furfural acts as a yeast inhibitor in quite small concentrations, as found by Lüers (36).

Instrumentation

Since there is no practical way of fitting a window to see into the extruder barrel, it is crucial to have reliable information from sensors which can be appropriately placed. Temperatures are given by a standard type of thermocouple manufactured commercially for the plastics and food industries, in a version which is fitted into an injection port of an extruder. A series of these "melt" thermocouples is fitted so as to sense the temperature along the reaction zone; in the NYU reactor, they are specified to protrude only 1/8 inch into the barrel, to minimize mechanical wear by the fibrous material. Each one gives a readout on the indicator display, and is calibrated periodically against a mercury-in-glass thermometer.

Pressure is likewise sensed by a transducer manufactured to fit into an extruder barrel, in this case specified to be made of corrosion-resistant Hastelloy as far as acid contact can occur; again, a display is given for each on the exciter/display unit, and calibration is carried out against a standardized Bourdon-type pressure gauge.

A combined version with a Type-J thermocouple and a pressure diaphragm in the one unit (Hastelloy version) is also available; this is the unit of choice. Actually, early experiments were done with only a single pressure transducer and a gauge indicator (Dynisco Model ER-478), which is much less sensitive than the digital indicator; however, it was kept in operation to provide a second pressure reading, and in fact movements of the needle sometimes give more information on transient pressure phenomena than does the digital display.

In this connection, it was hoped that more detailed data on the transient pressure changes within the extruder would give better understanding of such aspects as the ball valve discharge behavior and instability problems with the dynamic plug; so the pressure transducer output was connected to a high-speed recorder, normally used at the Westbury facility for combustion experiments, with mirror galvanometer and photo-sensitive chart paper. Some insights were gained, after which the operation was discontinued due to the cost of the large amounts of expensive chart paper needed.

Torque supplied by the extruder drive is the principal source of information on mechanical aspects of the operation, such as behavior of the dynamic plug, and a meter indicating this torque is standard equipment in the control panel; it reads percentage of full power (35 hp), with a selectable alarm point and overload cut-out.

Steam Supply

When the pilot plant extruder was first installed, steam was supplied by an electric boiler which had a rated maximum of 220 psi. This boiler essentially functioned to start up a hydrolysis run, and once the reaction was under way at some 450 psi, with the barrel heaters and shear stress supplying

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most of the energy requirement, it operated only as a back-up steam supply in case of a pressure drop. With this arrangement, difficulties were inevitably encountered in keeping the reaction temperatures and pressures as high and steady as desired, and it became clear that a higher-pressure steam supply was needed.

An appropriate boiler was obtained (Hydrosteam Industries, Inc., Alexandria, VA: Model STR=1638-6-4E), rated at 750 psi, and after various shakedown problems with it were overcome, it was found to improve dramatically the control of the hydrolysis process conditions.

While discharge from the reactor was controlled by the ball valve system, this boiler functioned after each opening of the valve to restore the pressure to the chosen value. With a large-bore steam line, this required about 1 second in the 20 second ball valve cycle; on the other hand, as compared to a smaller-bore line, in case of a dynamic plug failure, the large bore also gave a much bigger blow-back of extruder contents.

On changing over to the orifice system with its continuous discharge, this cycle of pressure drop and restoration, of course, disappeared, but it soon became apparent that the reaction pressure was still fluctuating over a longer cycle, and that this followed the steam pressure variations in the boiler (±50 psi). As supplied, an electro-mechanical diaphragm system was used to give the input signal to the step-controller for the boiler resistance heaters; a solid-state time-proportioning controller was installed to improve the situation. Unfortunately, this proved inoperable, and a regulating system was installed in the steam injection line instead. A Leslie pilot-operated pressure regulating valve stabilizes reaction temperature: the reactor pressure is the input signal to the pilot valve, which sends a proportional air signal to the steam regulating valve; steam flow is then throttled automatically to produce a pressure output constant to within 1%, or about 5 psi, which corresponds to ±1 F.

Energy Optimization

Clearly it is very important for the economics of the process to minimize energy consumption at every stage, and considerable efforts have been devoted to this. Where practicable, thermal insulation has been fitted to the high-temperature areas: piping is lagged, and the extruder barrel is wrapped in fiberglass blanketing.

Heat exchange has been applied at some stages, but this is essentially more a feature of an industrial operation, since in a research situation there is a problem of causing changes to quantities which are being measured or should be constant. The crammer feeder (Figure 18) is equipped with a jacket, and low-quality heat from the process could be used to pre-heat the "wet" feedstocks; in trials using low-pressure steam (20 psi) in the jacket, it was found that preheating was successful as long as the pulp was not dried out. By fitting part of the acid and steam injection lines concentrically, the acid was also preheated; but careful design is required to minimize erosion and corrosion.

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A test was made to see if steam injection alone could supply sufficient heat for the hydrolysis, as projected by calculations. Leaving the electric barrel heaters off, and setting the boiler at 450 psi, it turned out that the temperatures gradually dropped, implying that the thermal losses from the system as it stood were significantly greater than estimated. However, it is believed that the effects of more efficient insulation, better distribution of steam by injection at several locations, and the proportionally smaller heat losses for a larger commercial extruder would reduce these losses to a point near the calculated values. Subsequent experiments have all been performed with the barrel heaters on, although for the most part operating at a low proportion of their power during a run, i.e. essentially performing a thermally insulating function.

Accurate mass and energy balances are taken for most hydrolysis runs, the procedure being as follows. A volumetrically accurate screw feeder is used to introduce the cellulosic feedstock to the extruder; this is calibrated for each different feedstock sample by weight. Acid of known strength, and water when needed, are fed in volumetrically by positive displacement pumps, which are also calibrated by weight under an appropriate range of pressures. Steam is by far the most difficult flow to measure, both because of its nature and because of the relatively small scale of the operation. As the boiler is electrical, a kilowatt-hour meter is used to indicate the energy supplied, and an appropriate watt-transducer also is used to transmit it to the datalogger; these readings are mainly employed as a check on the most accurate value used in the actual mass and energy balance. This figure is obtained by measuring the water supplied to the boiler, by means of an electromechanical timer connected to the mass-calibrated feedpump; then combining this with the observed steam temperature and pressure to calculate the enthalpy required for heating it to the appropriate conditions. Mechanical energy, supplied by the extruder's variable speed DC drive, is measured by another kilowatt-hour meter and another watt transducer. Masses of the product collected, the vapors condensed, and any water squeezed from the feedstock at the feed end of the extruder are accurately measured at the end of a run on an electronic scale (Toledo digital readout load cell, platform type, Model 8134, with range 0 to 1200 ± 0.2 lb).

Results from all of these measurements give the specific energy consumption, and are used to draw up an energy balance diagram for the overall process, as outlined in Section 6(B).

Wear and Corrosion Monitoring

To check on their condition, the twin screws are removed periodically, and they and the inside of the barrel are examined, both visually and by means of a micrometer gauge. From this information, realistic estimates for the lifetime of components of an extruder can be made, and figured into the economic projections for the whole process.

Actual deterioration observed has been mainly due to accidents in the course of experimentation, and to poor initial choice of materials. For instance, at first some abrasion of the screw crests was found in the region just downstream from the plug, well before the acid and steam injection points;

it was deduced that this was solely of mechanical origin, and could be minimized by substituting bushings with hardened crests in this region.

Counteracting the tendencies to erosion and corrosion, a coating is observed to form on the screws and barrel around the reaction zone: black, hard, and strongly-adhering, it is presumed to be a resin of the phenol-formaldehyde type, produced by reaction between lignin components and decomposition products respectively, and it is believed to have a significant protective function for the metal. In the majority of cases, the coating is not removed when the screws are cleaned, but left in place for this reason. Much information could presumably be gained from a physical and chemical study of this coating, which may be of value commercially.

Residence Time Distribution

As mentioned earlier in regard to kinetics, the dilute acid reaction is quite "sensitive", both to residence time and temperature, for optimum yields. It is important to have the same brief residence time for all of the material, since if there is a wide distribution, some portions of the material could be under-hydrolyzed, while simultaneously other portions would be over-hydrolyzed, thus lowering the yield. Particularly during periods of operation where the ball valve discharge was in use and had cycle times of the same duration as, or sometimes longer than, the desired residence time, it was felt that such a wide distribution of residence times could be occurring.

Unfortunately, this is difficult to check directly. Some measurements were made by injecting a dye into the extruder, but these yielded only an average figure for the residence time. Another approach to obtaining a distribution measurement was the injection of iron filings, to be followed by a highly sensitive magnetic detector at the discharge region; these were not successful due to the limited time and equipment. With the development of the continuous discharge system, however, it was felt that the distribution had become much narrower, and that there was unlikely to be a serious problem any longer. Nevertheless, an exact measurement of the residence time distribution would be very valuable information, and it is intended to develop a method for this measurement as soon as possible.

Blockage-Clearing Techniques

Any time the torque load on the extruder motor is accidentally allowed to reach the cut-out level, there arises immediately a cleaning-out problem: usually there will be acid catalyst in the hot barrel as well as the cellulosic material, so possibilities of corrosion demand that the cleaning be done quickly. Experience gained in the pilot plant operation allows some principles to be set out.

If possible, the machine should be re-started and evacuated rather than be left stopped. To do this, feeding of the raw material into the extruder is halted while the injection rate of acid is increased. In the case of the ball valve discharge system, the hydraulic timer is over-ridden manually to give a series of rapid cycles. A solenoid switch has been added to the control panel which has the function of opening a valve to allow the full-

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pressure steam of the boiler (750 psi) directly into the extruder, instead of via the throttling valve (450 psi), thus providing a "steam purge" for both the steam injection line and the barrel. In addition, a capability has been added to reverse the extruder, by connecting a switch to change the field of the DC drive, thus allowing the material to be gradually backed out by the screws through the dewatering port; this is especially advantageous when using the orifice discharge system.

If all of these methods prove unsuccessful, the last resort is to set the barrel heaters at some 320 C and wait for the material to burn out.

Pulp Hydrolysis Results

Table 3 summarizes typical experimental runs for hydrolysis of wastepaper pulp. In examining the figures, several points must be borne in mind. Analytical results are subject to certain qualifications as far as absolute accuracy is concerned, as discussed in Section 5(A). However, in cases of similar reaction conditions, it is believed that interfering substances will have similar effects, so results are at least relatively accurate. Reaction-zone pressure was, at this stage, fluctuating over an undesirably wide range for two reasons. Firstly, the discharge of reacted material through the ball valve caused a sudden drop in pressure, and thus also in temperature, at each opening, lasting about 1/30 second, which was made up over several seconds during the closed part of the cycle, typically 20 seconds; this was later overcome by development of the truly continuous discharge through an orifice. Secondly, with reaction-zone pressures around 450 psi, the boiler at its maximum of 200 psi was of little help once a run was under way, either in making up the cyclic pressure drop just mentioned, or in allowing any significant freedom in selection of (average) reaction pressure and temperature; this situation was later improved by installation of a higher-pressure boiler.

Essentially, a conclusion was drawn from each experiment under its own set of conditions, leading to an equipment change or an engineering improvement. Thus, it is not possible to go too far in comparing results for a single variable, such as acid concentration, over the whole series. Closely controlled and systematic tests of this type were done later, for example in the case of hydrolysis results for specific sawdust types.

Figure 23 indicates the variation of glucose yield with acid concentration for continuous hydrolysis of pulp. Although it is also subject to some of the qualifying remarks made in regard to Table 3, the general trend is clear, and it should be particularly noted that substantial cellulose conversion is obtained in the extruder down to remarkably low acid strengths.

Sawdust Hydrolysis Results

Table 4 and Figure 24 show the variation of glucose yield with acid concentration for continuous hydrolysis of mixed hardwood sawdust. On comparing this curve with Figure 23 for newsprint pulp, it will be observed firstly that conversion begins to drop off below about 1% acid concentration, indicating lower accessibility of the alpha cellulose in the sawdust; and secondly that a slight drop in yield occurs above about 1.2% acid, indicating the onset of

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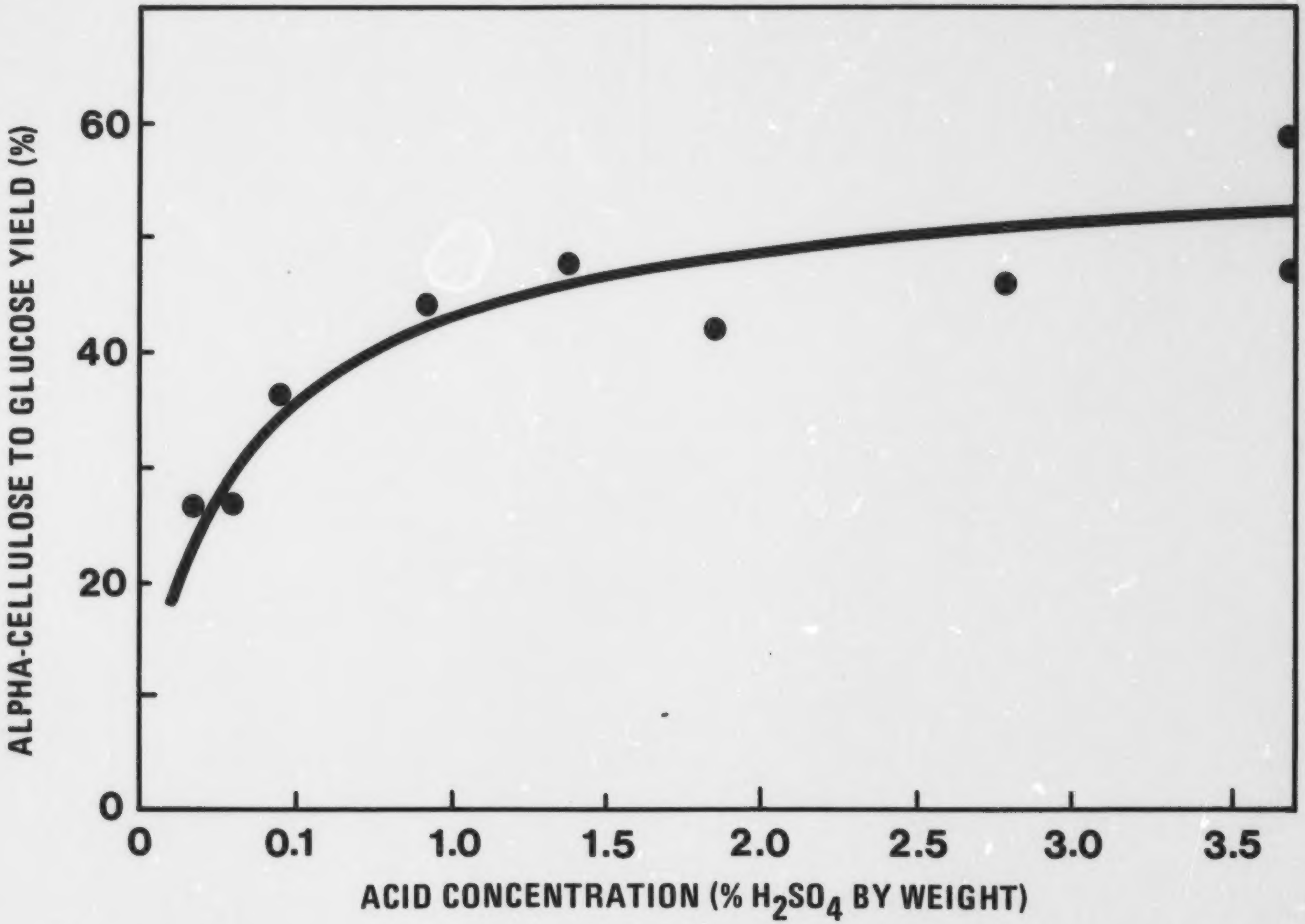
TABLE 3: RESULTS IN EXTRUDER HYDROLYSIS OF PAPER PULP

		REACTION CONDITIONS					ANALYSIS OF YIELD ALPHA CELLULOSE			
DATE	EPA NO.	ACID CONC.% (BY VOLUME)	ACID THROUGHPUT (ESTIMATE) ml/min	MASS(PULP) THROUGHPUT (ESTIMATE) gm/min	AVERAGE TEMPERATURE °F	AVERAGE PREESURE Psi	CONVERSION TO RED SUGARS % (DNS METHOD)	CONVERSION TO GLUCOSE % (NYU TEST)	CONVERSION SCHWARTZKOPF TEST	DEVIATIUN SCHW/NYU
2-6-79 - A	405	1.70	10.6	179	425	300	63.1	42.8	34.4	-19.6%
2-6-79 - B	406	1.70	10.6	179	450	325	61.0	43.5	37.7	-13.3%
2-16-79	407	1.8	8.0	179	438	325	58.2	43.3	37.7	-13.4%
2-23-79- A	408	0.85	5.4	179	442	310	56.7	38.8	33.0	-14.9%
2-23-79 -B	409	0.64	4.0	179	439	N.A.	58.9	43.6	37.9	-13.1%
2-27-79- A	410	0.43	2.6	179	439	360	57.7	41.2	35.8	-13.1%
2-27-79- B	411	0.21	1.4	179	446	360	46.7	34.0	36.4	+ 7.1%
2-27-79- A	412	1.70	10.6	179	457	360	86.3	55.0	48.3	-12.2%
3-2-79 - A	413	0.13	0.77	179	410	290	34.7	24.9	N.A	-
3-2-79- B	414	0.13	0.77	179	447	360	50.1	27.3	N.A	-
3-2-79 C	415	0.085	0.51	179	430	350	47.7	26.6	N.A	

Analysis Footnote

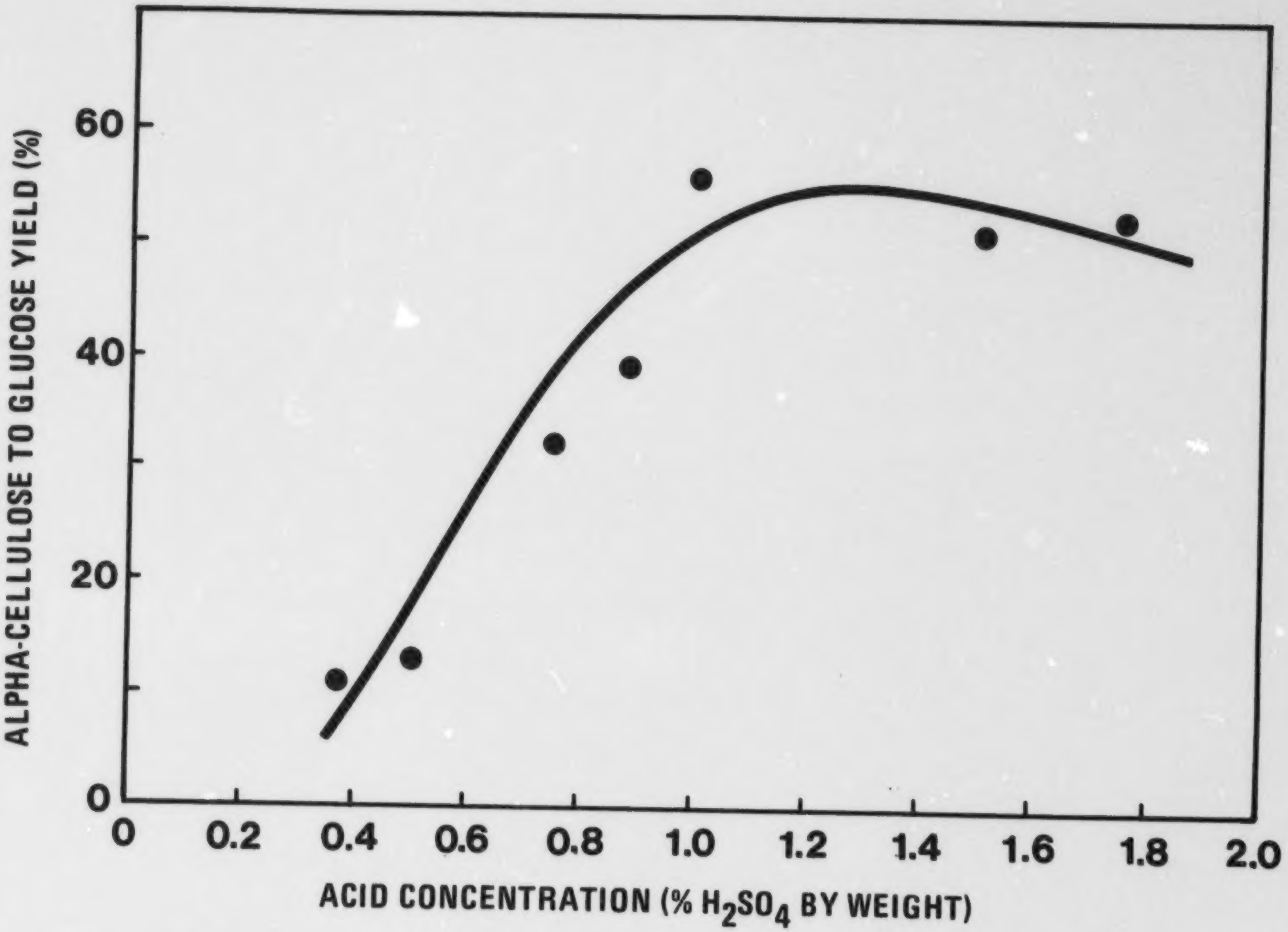
(i)Glucose: Samples were tested both in-house and at Schwarzkopf Laboratories in Queens, New York. Both groups use the AOAC Approved Schaffer-Somogyi Micro Method for analysis of glucose with $CuSo_4$ (Copper Sulfate) solution, and subsequent titration with $Na_2S_2O_3$ (Sodium Thiosulfate) solution. Discrepancies in the two results may arise because Schwarzkopf uses a more concentrated, and therefore less sensitive, solution of $Na_2S_2O_3$ (0.01N) relative to NYU (0.005N).

(ii)Reducing Sugars: The method used was the DNS Colorimetric method, and testing was done only in-house. The sample is reacted with 3, 5 Dinitrosalicylic Acid (DNS) Reagent, and a colorimetric determination performed on a spectrometer at 640 nm.



ALPHA-CELLULOSE TO GLUCOSE CONVERSION YIELD VS. ACID CONCENTRATION, NEWSPRINT PULP

FIGURE 23



ALPHA-CELLULOSE TO GLUCOSE CONVERSION YIELD VS.
ACID CONCENTRATION, SAWDUST

FIGURE 24

some decomposition of the glucose formed, presumably due to the effect of byproducts formed from components in the sawdust which are absent from the newsprint.

Following on from the results reported here, experiments on sawdust of individual wood species were later carried out as mentioned in the Description of Study (Section 3). These were performed at a stage when much closer control of reaction conditions had been attained, and analytical capabilities had been extended by HPLC to determining xylose and mannose as well as glucose; some results are shown in Figures 25-27.

TABLE 4. CONVERSION YIELD VS. ACID CONCENTRATION FOR CONTINUOUS HYDROLYSIS OF SAWDUST

Acid Concentration (H_2SO_4 % w/w)	Conversion Yield (Alpha-cellulose to glucose %)
0.37	10.7
0.50	13.3
0.75	32.0
0.88	39.3
1.00	56.0
1.50	51.3
1.75	52.7

Transfer to a Larger Facility

As the acid hydrolysis project expanded, the original facility at Westbury became inadequate in size as well as having difficulties with space heating and cooling. In late 1980, a move was made to a much larger area on the same site. This provides adequate space for discharge arrangements, downstream treatment, fermentation, isolated analytical lab, and work benches, as well as good temperature control. (A floor plan is shown in Figure 28.) As with the original installation, the extruder was set up on epoxy and concrete foundations by NYU personnel with guidance from Werner & Pfleiderer Corp.

C. SUMMARY

A considerable amount of information was obtained from experiments with batch hydrolysis reactors of two sizes, mainly in relation to pretreatments for increasing cellulose conversion efficiencies, and to establishing reaction conditions which would be a "base case" for a continuous process.

These conditions of high temperature and pressure in an acid environment

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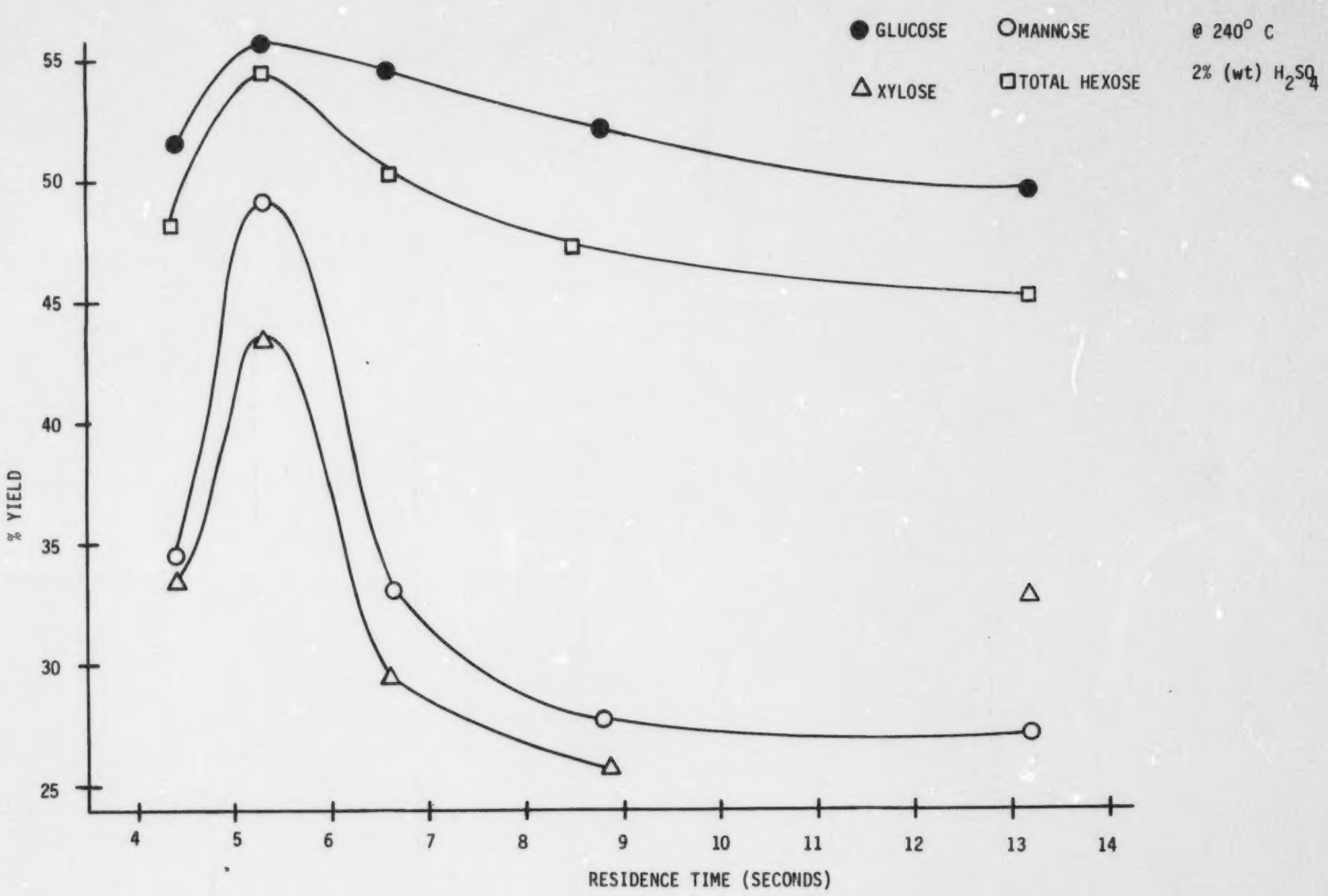

FIGURE 25: Yield vs Residence Time, Eastern White Pine

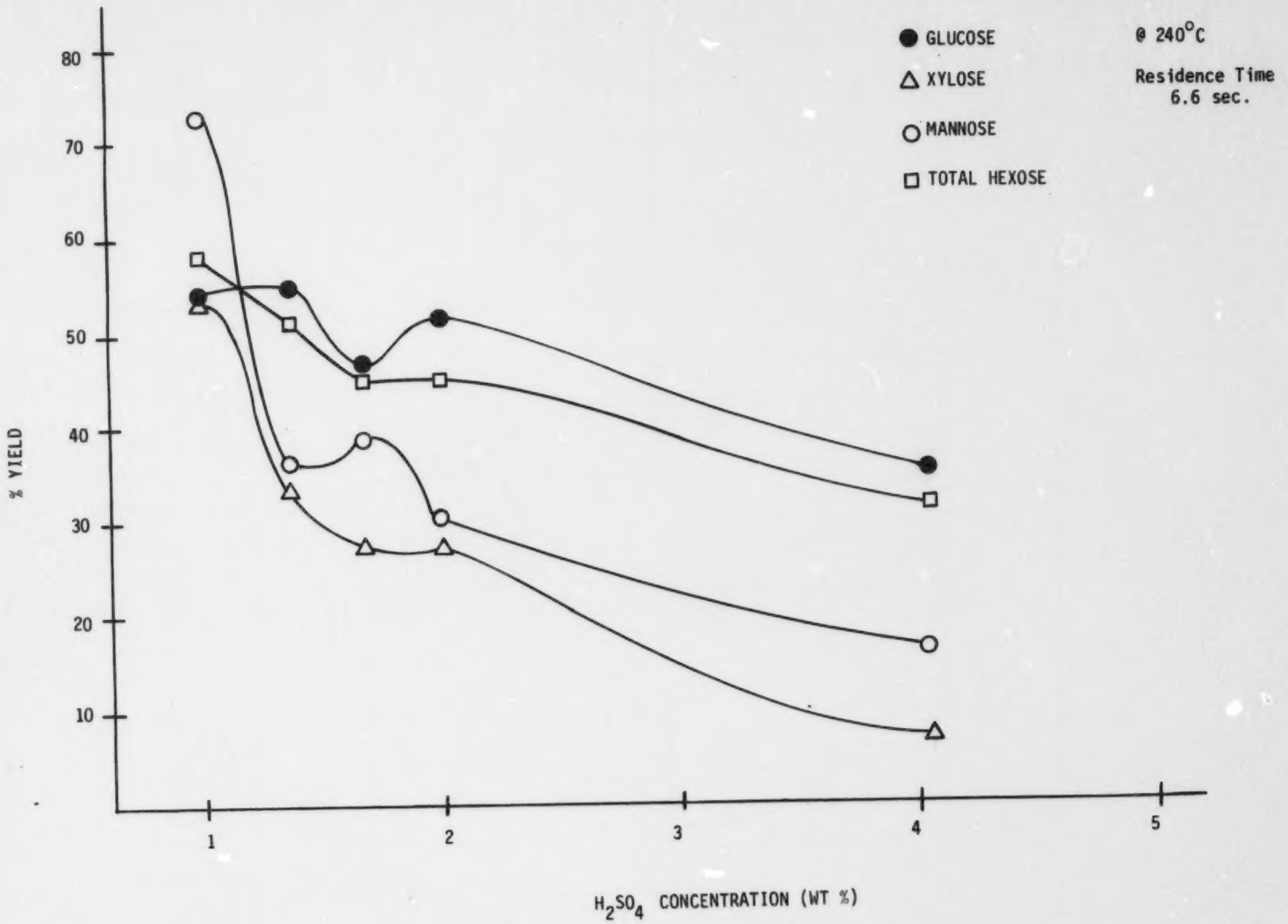

FIGURE 26: Yield vs Acid Concentration, Eastern White Pine

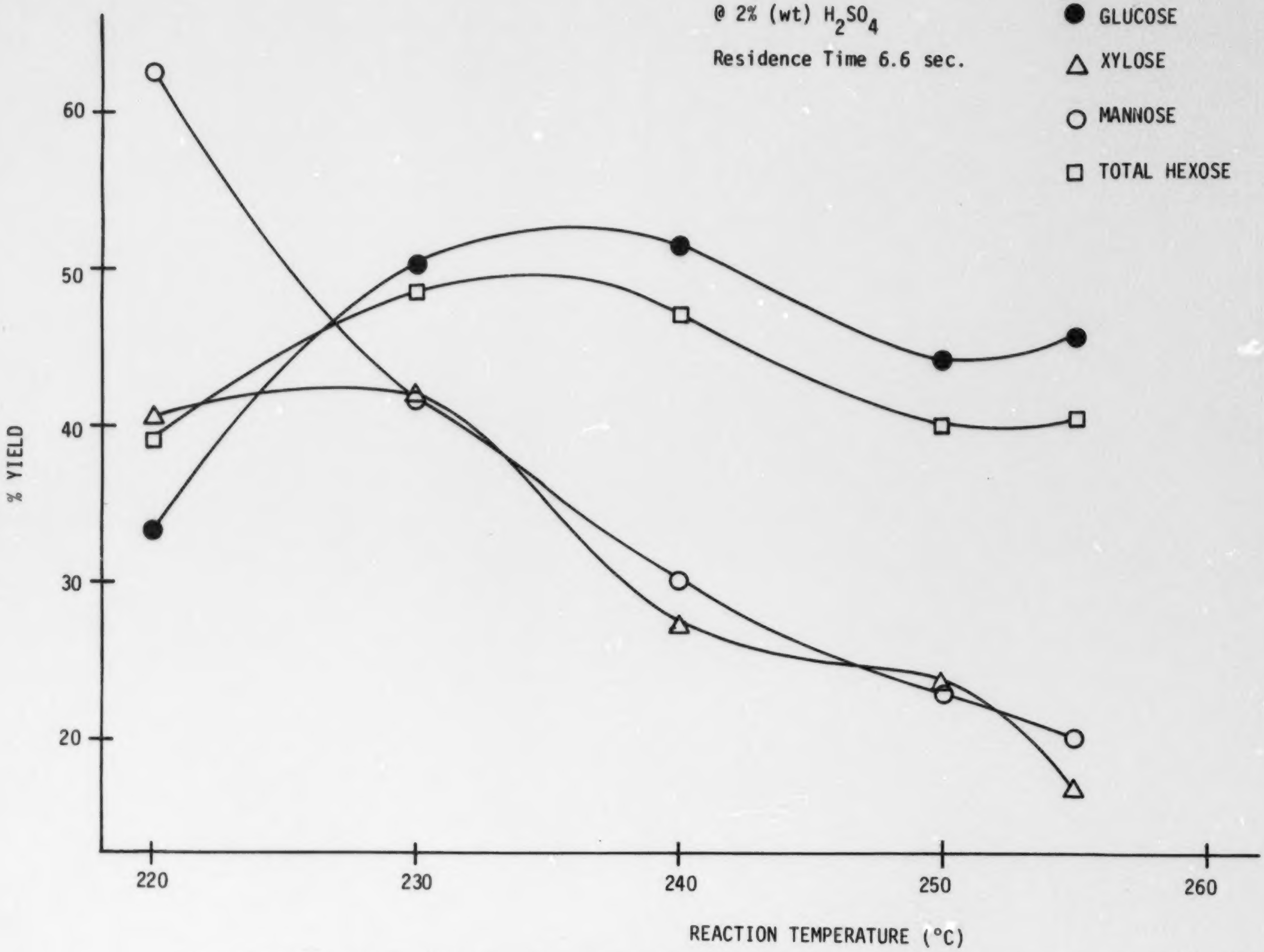

FIGURE 27: Yield vs Reaction Temperature, Eastern White Pine

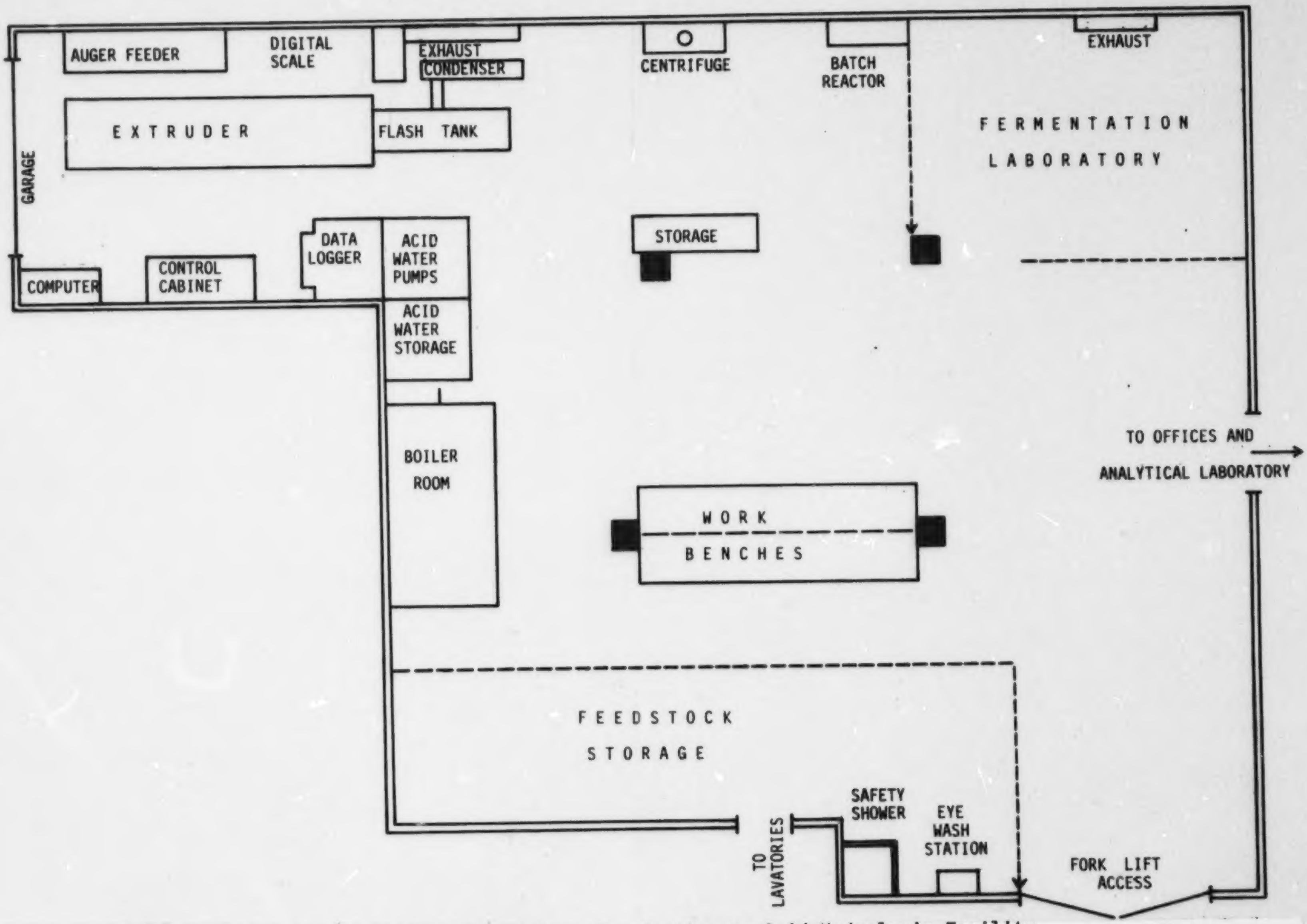
AUGER FEEDER
DIGITAL SCALE
EXHAUST
CONDENSER
CENTRIFUGE
BATCH REACTOR
EXHAUST
FERMENTATION LABORATORY
EXTRUDER
FLASH TANK
GARAGE
STORAGE
DATA LOGGER
ACID WATER PUMPS
COMPUTER
CONTROL CABINET
ACID WATER STORAGE
BOILER ROOM
TO OFFICES AND ANALYTICAL LABORATORY
WORK BENCHES
FEEDSTOCK STORAGE
SAFETY SHOWER
EYE WASH STATION
TO LAVATORIES
FORK LIFT ACCESS

FIGURE 28: Floor plan of New York University Continuous Acid Hydrolysis Facility

present many challenges, and the successful development of such a continuous process over the course of this contract comprised mainly the solution of a large number of problems of an engineering nature. Most important amongst these were the precise control of reaction temperature, pressure, and residence time, the feeding and discharge of material, and the minimization of energy consumption together with the maximization of glucose yields. Cellulosic feedstocks treated were principally waste paper, at 10% solids, and sawdust, at around 95% solids, and thus the versatility of the extruder concept of continuous cellulose hydrolysis was demonstrated.

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SECTION 5

GLUCOSE UTILIZATION

A. PRODUCT ANALYSIS

Initially, estimation of the amount of glucose produced in a hydrolysis experiment was done by sending samples to a commercial laboratory (Schwarzkopf Microanalytical Laboratory, Woodside, NY). However, the chemical nature of the product typically obtained from a cellulosic feedstock is fairly complex. In addition to the main product, glucose, other sugars such as mannose and xylose may be present from the hemicellulose in the feed. Also, oligosaccharides from incomplete hydrolysis, and decomposition products such as furfural derivatives and levulinic acid, together with substances from lignin breakdown such as phenols, make precise analysis essential. This complexity leads to considerable difficulties in analysis, compounded by the chemical similarity of the various sugars in the mixture: they have only minute differences in structure or conformation. After a while, it became apparent that the analytical results were inadequate, and it was decided that an in-house analytical capability should be developed.

A considerable body of work on this kind of analysis was done by the U.S. Forest Products Laboratory in the course of their acid hydrolysis investigations. Saeman (39) gives practical methods for determination of (i) total reducing sugars, using the method of Shaffer and Somogyi(40), involving reduction of a copper II complex to copper I and subsequent titration with sodium thiosulfate; (ii) fermentable sugars, using the method of sorption of sugar on yeast (e.g., 41); and (iii) ethanol, using the Westphal balance method. Starting from this and other related work, "wet chemistry" techniques were developed in the NYU labs for analysis of hydrolyzates. Most effort was directed towards the Shaffer-Somogyi analysis mentioned above, and the DNS method. The latter is essentially reaction with a 3,5-dinitrosalicylic acid reagent followed by a spectrophotometric determination at 640 nm; it gives good results for a feedstock with a low hemicellulose content, but otherwise becomes unreliable.

In the process lab, a quick and convenient approximate indication of glucose was obtained with Testape. This is a small roll of test paper manufactured for medical uses, impregnated with a preparation of the enzyme glucose oxidase, so that a minute after contact with a solution, it changes color from yellow to a shade of green which corresponds to the glucose content of the solution, a printed color chart being provided for comparison. If very strong, the solution needs to be diluted to the working range of the Testape.

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To find the total glucose potentially available in an original cellulosic feedstock sample, the quantitative saccharification procedure of Saeman (42) was carried out: this essentially involves a slow, careful, and complete breakdown of the cellulose with sulfuric acid. Conversion yields can then be calculated as the ratio of glucose actually obtained to that potentially available.

An instrumental method was also employed for glucose determination (Beckman Instruments, Inc., Fullerton, CA: Glucose Analyzer II). This is based on an enzymatic procedure, and gives good results for samples within certain limitations.

Undoubtedly, the method of choice for analysis of complex mixtures such as these hydrolyzates is chromatography, in which the components are unequivocally separated prior to determination. Examination of commercially available equipment for HPLC (High Performance Liquid Chromatography) was commenced, as well as discussions with personnel in other laboratories, but it was not until after the expiration of the EPA contract which is the subject of this report, that the NYU Lab was able to purchase and use an HPLC set-up. It may be mentioned in this connection that results from HPLC analyses confirmed those from the Beckman instrument to within 2%.

B. GLUCOSE RECOVERY

The extrusion process produces a dark, viscous mud composed of unreacted cellulose and lignin, together with glucose, acid, water up to 50% by weight, and soluble decomposition products, such as phenols, furfurals, and levulinic acid. The composition of the mud depends on the particular feedstock and reaction conditions. Handling of it is described in Rugg (51);see Table 5.

To recover the glucose from the mud, experiments have shown the best method to be a perforated-bowl centrifuge with spray-washing and semi-continuous discharge of solid cake. As wash water is injected, liquid centrifugate containing the soluble glucose is continuously spun out, while the centrifuge cake is maintained at a nearly constant solids content. To efficiently extract glucose, more wash water is required, resulting in more dilute final solutions. Figure 29 illustrates this relationship for actual trials using hydrolyzate from a sawdust feedstock and a Lavin model 1120A centrifuge, which produces 30% cake at 2000 g's. The other two curves, generated by a computer simulation, are for 40 and 50% solid cake, respectively, which should be possible with advanced centrifuge technology. Points marked by triangles represent early trials, while crosses represent more recent results obtained in the course of preparing samples for the fermentation experiments described in the next section and Appendix D.

Another alternative being evaluated is the direct fermentation of the extrudate, including simultaneous enzymatic saccharification of the residual cellulose (see next section on fermentation). Subsequent distillation of this mash may lead to significant economic advantages.

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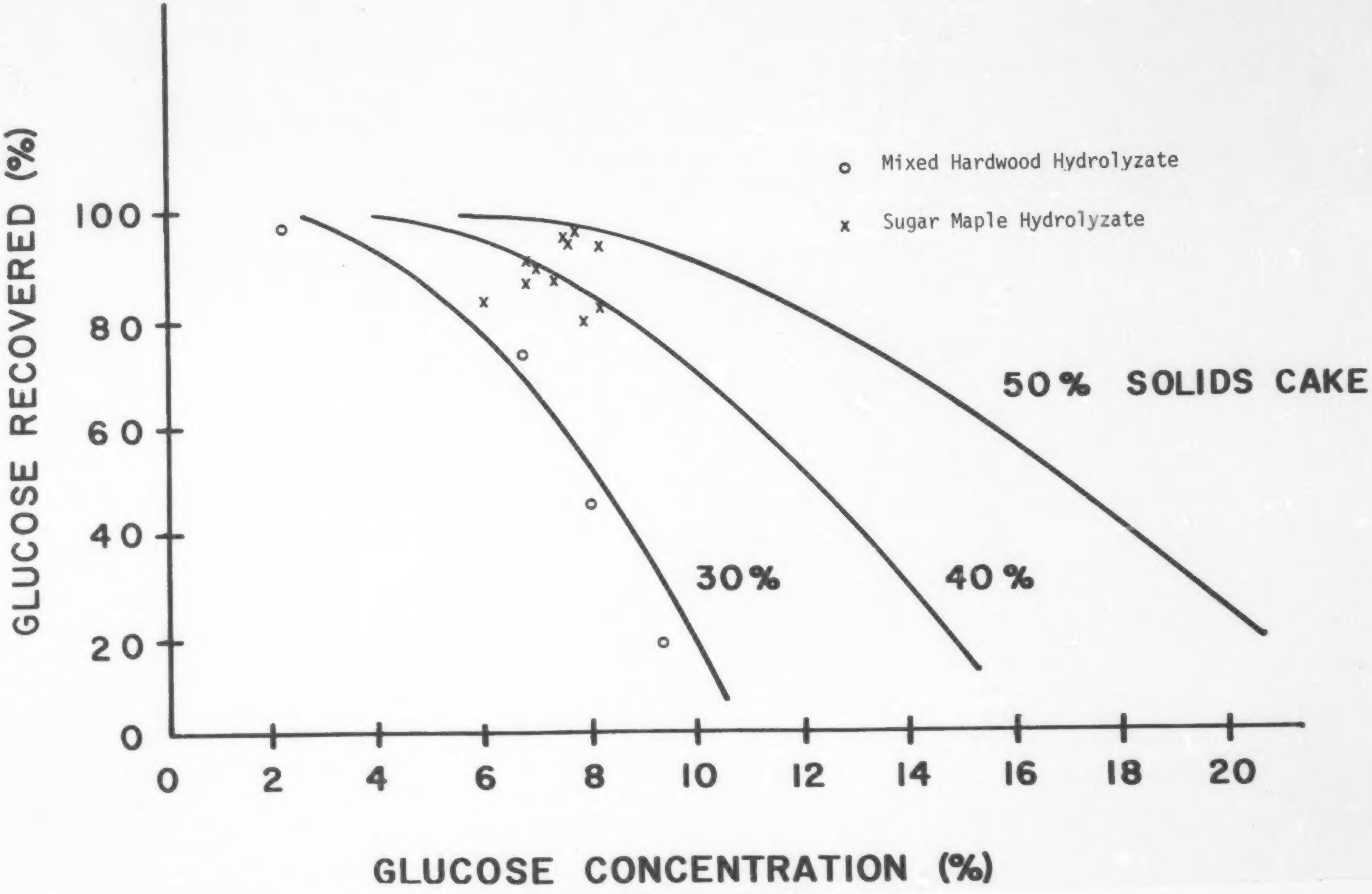

FIGURE 29: Centrifuge: Final glucose concentration vs % recovery

TABLE 5

SEPARATION TRIALS ON SUGAR MAPLE HYDROLYZATE
(All Weights in LBS)

	HYDROLYZATE				SOLIDS CAKE				CENTRIFUGATE				
SAMPLE NUMBER	WEIGHT	GLUCOSE CONCENTRATION	MOISTURE	TOTAL GLUCOSE	WEIGHT	GLUCOSE CONCENTRATION	SOLIDS	TOTAL GLUCOSE	WEIGHT	SOLIDS	TOTAL GLUCOSE	GLUCOSE RECOVERY	GLUCOSE CONCENTRATION
117	145.0	6.87	77.6	9.96	23.8	3.4	53.7	0.81	121.2	15.7	9.45	94.8	7.8
118	144.8	8.10	72.7	11.72	26.4	3.4	55.8	0.89	118.4	16.3	9.70	82.7	8.2
119	118.8	6.85	73.6	8.13	19.6	4.1	49.8	0.80	99.2	18.6	7.93	97.5	8.0
121	251.8	7.37	75.2	18.55	40.4	3.5	54.2	1.41	211.4	18.2	17.75	95.7	8.4
122	150.4	6.90	78.2	10.37	23.8	3.5	52.5	0.83	126.6	15.4	10.00	96.4	7.9
123	147.6	7.57	84.8	11.17	32.4	3.7	49.6	1.19	115.2	18.2	9.10	81.5	7.9
125	59.0	6.63	83.6	3.91	9.8	3.3	52.8	0.32	49.2	15.4	3.44	87.9	7.0
126	136.6	7.27	85.4	9.93	21.4	3.2	50.8	0.68	115.2	14.3	8.64	87.0	7.5
127	130.0	6.47	78.7	8.41	19.8	3.5	53.8	0.69	110.2	17.0	7.71	91.6	7.0
130	145.4	6.60	81.6	9.59	24.2	3.2	52.9	0.77	121.2	14.6	8.72	90.0	7.2
131	96.2	6.06	86.0	5.83	16.8	2.4	54.0	0.40	79.4	13.7	4.92	84.4	6.2

C. FERMENTATION AND BIOCONVERSION

Good accounts of past work on fermentation of hydrolyzates are available in Lüers (36,38), Saeman (44), and Hajny (13). Suitable conditions are generally in the range of pH 4 to 5, sugar concentrations of 10 to 15% by weight, temperatures of 30 to 40 C, a higher-than-normal yeast concentration up to 2% by volume, oxygen concentration of 0.07 mm Hg, some provision for agitation and foam control, and perhaps low pressure for continuous removal by distillation of the alcohol as formed.

Hydrolysis by-products have been observed to inhibit the action of the yeast. The principal toxins are believed to be lignin fragments, particularly pinene, menthol, borneol, and tannin, together with decomposition products of the sugars such as furfurals, formic acid, and levulinic acid; other toxic substances come from extraneous material in the feedstock, and from corrosion of equipment. Hajny (13) points out that saccharification processes have always been optimized for sugar yields rather than for fermentability of solutions.

Various methods have been proposed (44,45) to reduce the inhibition:

- acclimation of the yeast -- over a number of transfers, from 4 in some cases to 15 in others, the productivity of the organism is found to increase up to a plateau level;
- high yeast concentration -- simply inoculating a larger-than-normal amount of yeast has been shown to help sustain fermentation;
- neutralization at high temperature -- by releasing the reaction mixture to an intermediate temperature of 140 C, two advantages are obtained: the neutralization product calcium sulfate has minimum solubility, and the fermentability of the solution increases;
- adding a reducing agent -- for example, sulfur dioxide or sodium thiosulfate;
- adding alkali to pH 10, filtering, then re-acidifying to pH 6;
- adsorption on activated charcoal or ion-exchange resin;
- membrane separation;
- precipitation with proteins;
- steam stripping -- to remove volatile inhibitors;
- extraction or sulfide precipitation;
- "resinification" -- Scholler's procedure (33) wherein the solution is thickened to specific gravity 1.4, then held at 90 C for several hours, whereupon it becomes much easier to separate.

Although the inhibitory nature of the hydrolyzate requires one or more of these remedies to be applied, it also has the advantage that the chance of contamination by wild organisms is reduced.

Studies have been undertaken by various groups to evaluate the fermentability of the NYU product. In the New York City laboratories of NYU, initial experiments carried out on hydrolyzate from the batch reactor were aimed at developing a system with immobilized yeast cells. However, this work was inconclusive with the time and manpower available, and had to be abandoned.

At the Westbury laboratories of NYU, the first trials done with hydrolyzate from the continuous process were for waste paper pulp feedstock, as mentioned in section 4(B). These were done in 250 ml conical flasks, equipped with air traps. Yeast and nutrients were added, but no detailed measurements were set up: fermentation was followed by observing carbon dioxide bubbles escaping. It was concluded that the brewers' yeast used was capable of acclimating to whatever inhibitants were present in the pulp hydrolyzate, and that properly controlled bench-scale fermentation and perhaps yeast growth experiments should be undertaken.

Preparations for such experiments were begun, but not completed within the period of this EPA contract. However, a series of fermentation trials were later successfully carried out, and some results are given in Rugg (53) and Appendix D.

As mentioned in the Introduction (Section 1), there exist many possibilities for bioconversion of the glucose produced other than yeast fermentation to ethanol. Two alternative routes have been tested so far on the NYU hydrolyzate. In Cave Spring, Georgia, the Davis Core and Pad Company is cooperating with Dr. Lars Ljungdahl of the University of Georgia to develop processes for using the thermophilic bacterium Clostridum thermocellum, on separated sugar solutions and on the raw extrudate. In the case of the raw product, the unconverted cellulose as well as the sugar is utilized by the organisms, some of which can function at a pH as low as 3. Results obtained to date have been very promising, and some details are given in Appendix E.

Working on sugar solutions separated from the NYU acid hydrolyzate, methane fermentation studies have been carried out by Dr. V.R. Srinivasan of Louisiana State University. Most of this work concerns optimizing the yield with mixed cultures of methanogenic organisms extracted from both cow's rumen and a sewage digestor, and some details of the results may be found in Appendix F. Additional experiments are underway in Europe, Canada, and the United States on fermentation of hydrolyzates from the NYU process.

SECTION 6

MAXIMUM USE OF FEEDSTOCK

A. MATERIAL FLOW AND HEMICELLULOSE UTILIZATION

In order both to understand properly the pilot plant process and to produce realistic plant designs and cost estimates for larger-scale operations, it is essential to have accurate values for the flow of materials and energy in the system. One of the major continuing thrusts of NYU work has been the development and improvement of methods for monitoring all aspects of the pilot plant in order to arrive at reliable material and energy balances.

An analysis for the carbohydrate and lignin fractions of representative hardwood sawdust is given in Table 6. Material flow charts for hydrolysis based on this type of analysis are given in Figures 30 and 31, from Rugg (52); a more detailed chart for the overall process is also given in Section 7, Environmental Considerations. It will be noticed that the second flow chart shows a much higher conversion (80% vs 58%) of the hemicellulose fraction to monosaccharides; this is achieved by a 2-stage process. Because of its relatively higher degree of molecular disorder and thus accessibility, the amorphous hemicellulose reacts to form sugars under mild conditions, and thus a portion of it is lost to decomposition products when subjected to the severe conditions required for the conversion of crystalline α-cellulose to glucose.

TABLE 6. ANALYSIS OF MIXED HARDWOOD SAWDUST (55)

	wt%, dry basis
α-Cellulose (crystalline)	45
Hemicellulose Glucan	4
Mannan	4
Xylan	17.5
Others	8.5
Lignin	21
Total	100

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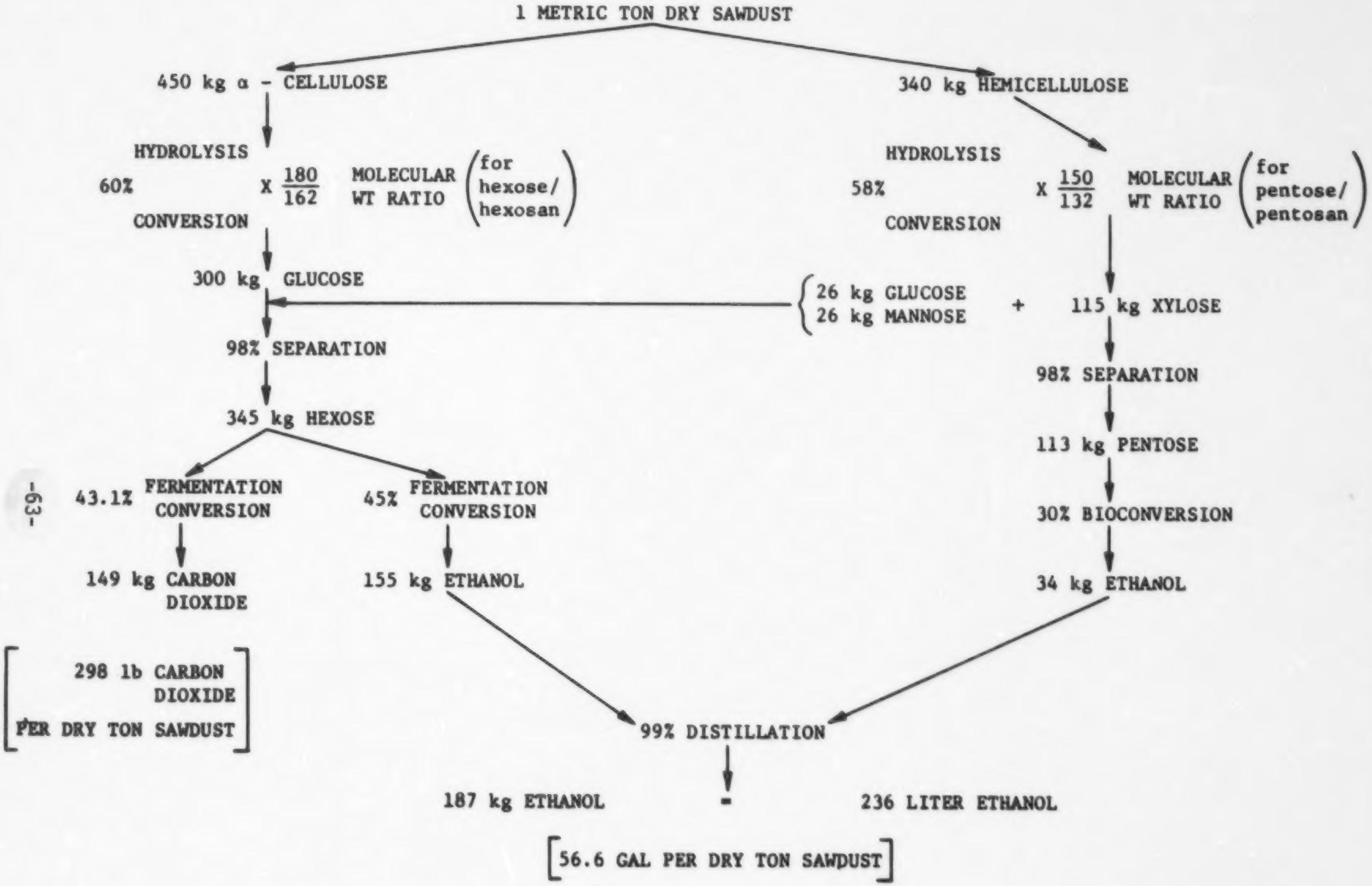
1 METRIC TON DRY SAWDUST
450 kg α - CELLULOSE
340 kg HEMICELLULOSE
HYDROLYSIS
60%
CONVERSION
X 180/162
MOLECULAR WT RATIO (for hexose/hexosan)
HYDROLYSIS
58%
CONVERSION
X 150/132
MOLECULAR WT RATIO (for pentose/pentosan)
300 kg GLUCOSE
26 kg GLUCOSE
26 kg MANNOSE
+
115 kg XYLOSE
98% SEPARATION
345 kg HEXOSE
98% SEPARATION
113 kg PENTOSE
43.1% FERMENTATION CONVERSION
45% FERMENTATION CONVERSION
30% BIOCONVERSION
149 kg CARBON DIOXIDE
155 kg ETHANOL
34 kg ETHANOL
298 lb CARBON DIOXIDE PER DRY TON SAWDUST
99% DISTILLATION
187 kg ETHANOL
=
236 LITER ETHANOL
56.6 GAL PER DRY TON SAWDUST

FIGURE 30: Material Flow for Single-Stage Process

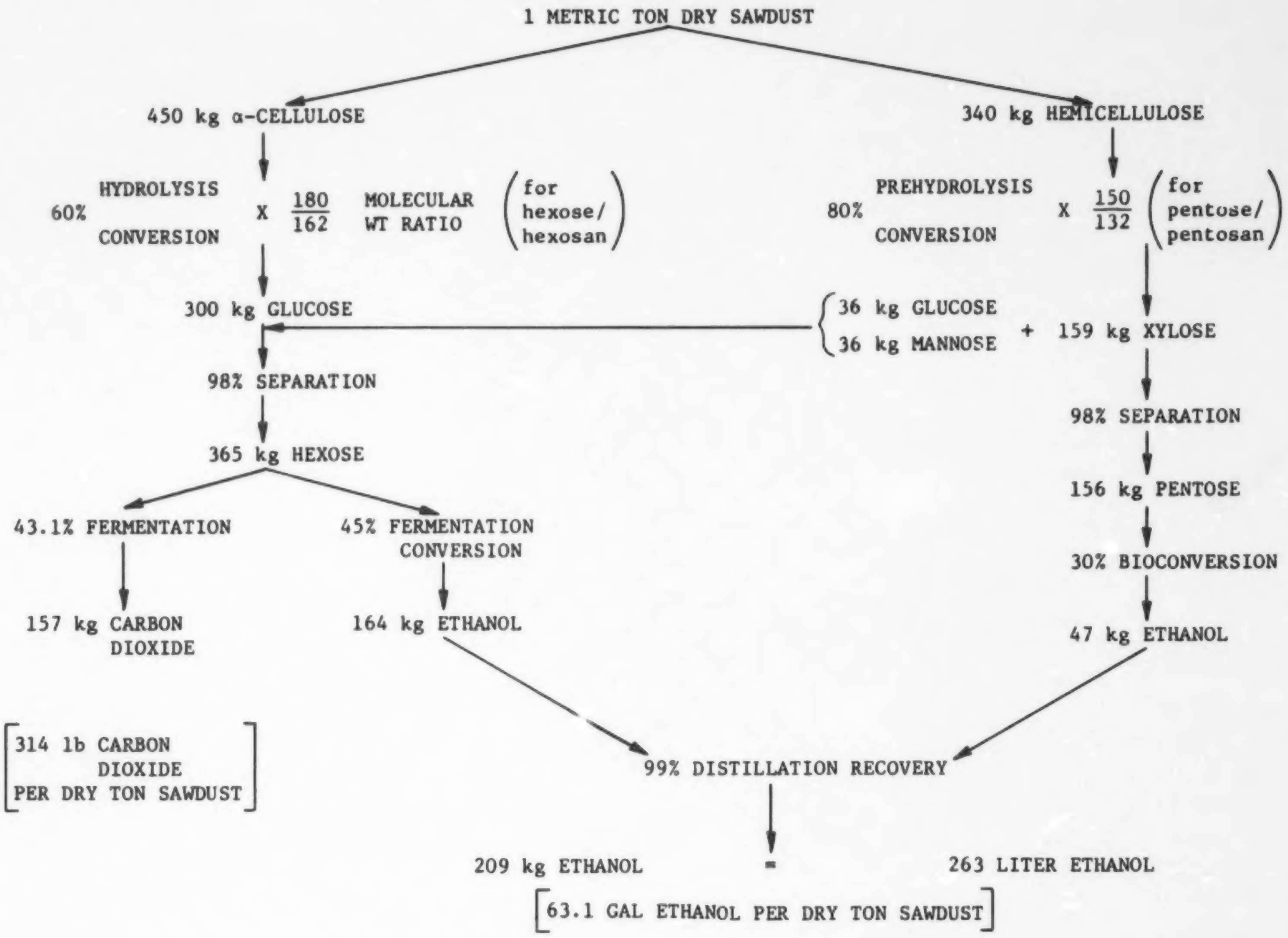
1 METRIC TON DRY SAWDUST
450 kg α-CELLULOSE
340 kg HEMICELLULOSE
60% HYDROLYSIS CONVERSION
X 180/162
MOLECULAR WT RATIO
(for hexose/hexosan)
80% PREHYDROLYSIS CONVERSION
X 150/132
(for pentose/pentosan)
300 kg GLUCOSE
36 kg GLUCOSE
36 kg MANNOSE
+ 159 kg XYLOSE
98% SEPARATION
365 kg HEXOSE
98% SEPARATION
156 kg PENTOSE
43.1% FERMENTATION
45% FERMENTATION CONVERSION
30% BIOCONVERSION
157 kg CARBON DIOXIDE
164 kg ETHANOL
47 kg ETHANOL
314 lb CARBON DIOXIDE PER DRY TON SAWDUST
99% DISTILLATION RECOVERY
209 kg ETHANOL
=
263 LITER ETHANOL
63.1 GAL ETHANOL PER DRY TON SAWDUST

FIGURE 31: Material Flow for Two-Stage Process

Therefore, in order to extract the maximum carbohydrate value from cellulosic residues, it has been proposed to carry out a two-stage hydrolysis, in which the hemicellulose fraction is prehydrolyzed and extracted prior to an α-cellulose hydrolysis.

Exploratory pilot plant trials of such a process have been carried out at NYU, confirming the laboratory results of other workers such as Prof. R.P. Chambers at Auburn University, Alabama. These trials were technically successful, but the financial projections made from them, as given in Section 8 on Economics, indicate that at this stage the extra yield achievable by two-stage hydrolysis does not justify the additional expenditure required to obtain it.

B. ENERGY BALANCE

It is recognized that achievement of high energy efficiency for the overall operation is doubly important because one of the misguided criticisms sometimes levelled at alcohol or gasohol fuel processes is that they "consume more energy than they produce". This criticism is misguided because it is in most cases not true, and irrelevant when the main aim is to provide liquid fuel to replace imported oil.

Section 4(B) outlines the efforts being made to reduce energy consumption in the NYU process, and gives the experimental procedure for obtaining a mass and energy balance for hydrolysis. Such measurements taken for representative runs are used to give realistic projections for an industrial operation, as shown in the energy balance diagram, Figure 32.

Optimum use of the ligno-cellulosic residue from the process as boiler fuel is regarded as of great importance until a higher use for the lignin as an economic source of chemicals is demonstrated (see following subsection on lignin utilization). It is assumed in this scheme that residual lignin is utilized as boiler fuel and that a cogeneration arrangement produces all the electrical and steam power required for the plant. While some variations in practice could be made to the scheme, such as a final vacuum stage for the turbine or a series of steam bleeds instead of the low-pressure steam manifold, these would not make a significant difference to the overall efficiency. As can be seen, the NYU process has a net energy surplus in the form of electric power for sale, as well as producing the liquid fuel (or chemical feedstock) ethanol.

C. LIGNIN UTILIZATION

An aspect which could make a significant improvement to the cost-effectiveness of the plant operation is the utilization of the enormous potential value that lies in the lignin "binder" fraction (around 25% of dry weight) of woody plants. While intensive research is being carried out on ways to exploit individual aromatic chemicals from this complex polymeric material, it appears that at present the most likely route to be taken will be processing of the material to a soluble form, in which its aromatic chemical nature allows it to undergo electrophilic substitution, so that it may be nitrated, halogenated, hydroxylated, or coupled with diazonium salts (48).

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ENERGY BALANCE FOR NYU ACID HYDROLYSIS PROCESS

BASIS: HARDWOOD FEEDSTOCK

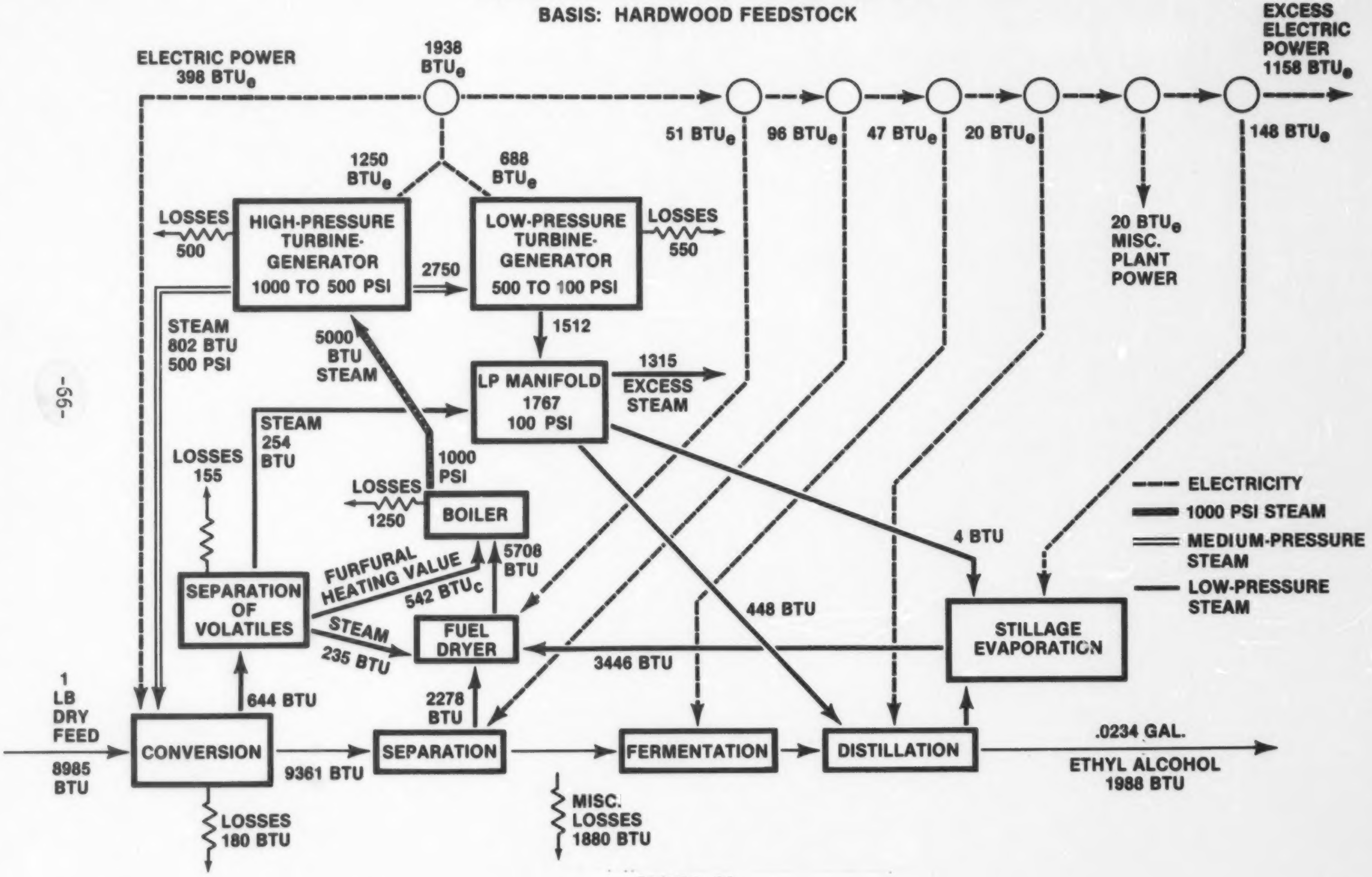
ELECTRIC POWER 398 BTU$_e$
1938 BTU$_e$
EXCESS ELECTRIC POWER 1158 BTU$_e$
51 BTU$_e$
96 BTU$_e$
47 BTU$_e$
20 BTU$_e$
148 BTU$_e$
1250 BTU$_e$
688 BTU$_e$
LOSSES 500
HIGH-PRESSURE TURBINE-GENERATOR 1000 TO 500 PSI
2750
LOW-PRESSURE TURBINE-GENERATOR 500 TO 100 PSI
LOSSES 550
20 BTU$_e$ MISC. PLANT POWER
STEAM 802 BTU 500 PSI
5000 BTU STEAM
1512
LP MANIFOLD 1767 100 PSI
1315 EXCESS STEAM
STEAM 254 BTU
LOSSES 155
1000 PSI
LOSSES 1250
BOILER
ELECTRICITY
1000 PSI STEAM
MEDIUM-PRESSURE STEAM
LOW-PRESSURE STEAM
4 BTU
FURFURAL HEATING VALUE 542 BTU$_c$
5708 BTU
SEPARATION OF VOLATILES
STEAM 235 BTU
FUEL DRYER
448 BTU
STILLAGE EVAPORATION
3446 BTU
1 LB DRY FEED 8985 BTU
644 BTU
2278 BTU
CONVERSION
9361 BTU
SEPARATION
FERMENTATION
DISTILLATION
.0234 GAL. ETHYL ALCOHOL 1988 BTU
LOSSES 180 BTU
MISC. LOSSES 1880 BTU

FIGURE 32

Comparative studies are being made by Glasser (49) on lignin residues from various cellulose conversion processes, both biological and chemical. These indicate that for the NYU process, it is easy to procure a homogenous lignin-rich solid fraction, with good solubility in alkali or dioxane: easier in fact than for the residues from bioconversion as well as from other non-biological conversions. This is an unexpected result which, aside from its scientific interest, suggests some favorable economic projections. For example, if a cellulose hydrolysis plant were to sell 25% of its lignin residue while using the rest for fuel, at a price say 20% below that of lignin from the Kraft process, with which it would have to compete, this would allow a considerable offset in the production cost of ethanol: for feedstock at $0 or $30 per ton, using the costs in Section 8 on Economics, but neglecting the electricity byproduct credit, there would be a reduction respectively from $0.51 or $1.17 per gallon to some $0.21 or $0.48 per gallon. Figure 33 reproduced from Professor Glasser's report (49) shows the effect of market price of co-produced lignin on ethanol selling price for various cellulose to ethanol systems.

Market size for lignin products is also being studied by Glasser. Lignin can be used as an extender for thermosetting resins, or even directly as a substitute. For the four basic types of thermosetting adhesive used in forest-product industries, namely urea-formaldehyde, phenol-formaldehyde, melamine-formaldehyde, and isocyanates, the total U.S. market is some 4 billion lb/year. Table 7 shows the individual market sizes and market values for three scenarios for incorporation of lignin at 25, 50 and 75% replacement levels. One difficulty in regard to such proposals for exploiting the lignin fraction of cellulosics is that the product may have a dark color. It appears, however, that this is more of a marketing problem than a technical one. In New Zealand, for example, a black adhesive has been successfully marketed in particle board, employing a bark extract substitute in phenolic resins; also, work is being done by Boise Cascade Corp. in Idaho on similar lines employing "black liquor" from pulping operations.

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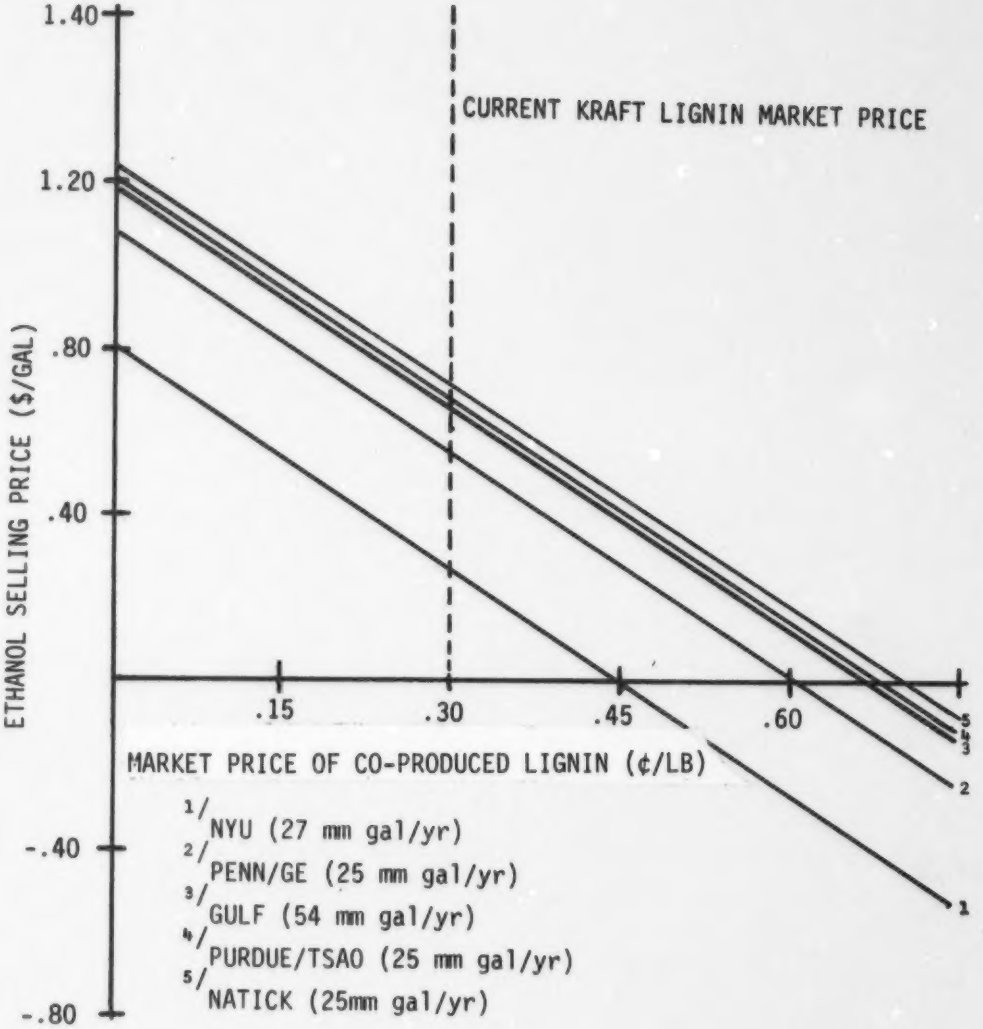

FIGURE 33: Effect of market price of co-produced lignin on ethanol selling price.

TABLE 7

MARKET SIZES AND VALUES OF THERMOSETTING RESINS AT VARIOUS REPLACEMENT LEVELS WITH LIGNIN

	PRODUCT CATEGORY				
AMOUNTS/VALUES	PHENOL-F	MELAMINE-F	ISOCYANATE	UREA-F	TOTAL
Total U.S. Production (MM lbs, dry wt. basis, pa)	1,400	235	1,000	1,365	4,000
Price $/lb	0.44	0.77	1.00	0.20	
Total Market Value (MM $/yr)	616	181	1,000	273	2,070
Scenario A: 25% Replacement Level with Lignin					
Total Lignin consumption (MM lbs/yr)	350	59	250	341	1,000
Total Market Value of Lignin @ 25¢/lb (M $/yr)	87,500	14,750	62,500	85,250	250,000
Scenario B 50% Replacement Level with Lignin					
Total lignin consumption (MM lbs/yr)	700	118	500	682	2,000
Total Market Value of Lignin @ 25¢/lb (M $/yr)	175,000	29,50	125,000	170,500	500,000
Scenario C: 75% Replacement Level with Lignin					
Total Lignin consumption (MM lbs/yr)	1,050	177	750	1,023	3,000
Total Market Value of Lignin at @25%/lb (M $/yr)	262,500	44,250	187,500	255,750	750,000

SECTION 7

ENVIRONMENTAL CONSIDERATIONS

A comprehensive discussion of the nature and treatment of the wastes anticipated from an industrial-scale plant is given in Reference 46. For a plant of capacity 2000 tons feedstock per day, or 25 million gallons of 95% ethanol per year, a detailed material balance is as follows (Figure 34 and Table 8).

Waste streams are generated from the separation of the hydrolyzate. The filter cake from the centrifuge contains lignin, unreacted cellulose, $CaSO_4$ from lime neutralization, glucose, decomposed sugars, and entrained water. Some 1470 tons per day of this residue will require treatment: dewatering provides a clean-burning, high heating-value fuel to meet process demand for steam. Emissions from combustion of this residue are compared to those from combustion of coal in Table 9. For all three of the feedstocks, sulfur (SO_x) emissions are lower than for coal; on the other hand, emissions of particulates, carbon monoxide, and hydrocarbons are higher for wood and for the agricultural residue bagasse, though not for municipal solid waste. No difficulties are foreseen in dealing with these emissions by conventional methods.

In the liquid fraction, sugar decomposition products are discharged from the reactor along with the non-fermentable sugars. This is a waste stream with high BOD (biological oxygen demand), requiring secondary biological treatment. Specifically, Converse et al. (47) measured the five day BOD of an unfiltered sample of fermentor effluent as 6,550 ppm, and of a filtered sample as 6,070 ppm. (Currently, the Federal requirement for BOD is 100 ppm.) The standard test for BOD had to be modified due to the presence of ferrous and nitrate ions; ferrous ions present in the stream from corrosion of equipment and nitrate ions formed by degradation of proteins during fermentation both interferred with test results. Again, no problems are anticipated in handling the effluent with normal methods. From the distillation operation, the principal waste stream is the residue discharged from the bottom of the beer still, some 6,700 tons per day at 3 to 4% solids and a high BOD (18,000 to 22,000 ppm); these beer still bottoms contain yeast not recaptured for recycle, sugars, and mixed alcohol products, typical compositions being listed in Table 10.

After filtration, the solids portion is often sold as cattle feed supplement (DDG -- Distillers Dried Grains); the protein value of the feedstock remains essentially unchanged throughout processing. Since crop residues do not represent a good protein source, the stillage serves as a medium on which to grow yeast; the yeast is mixed with molasses and fermentation proceeds aerobically. Recovery of the beer still bottoms will not significantly

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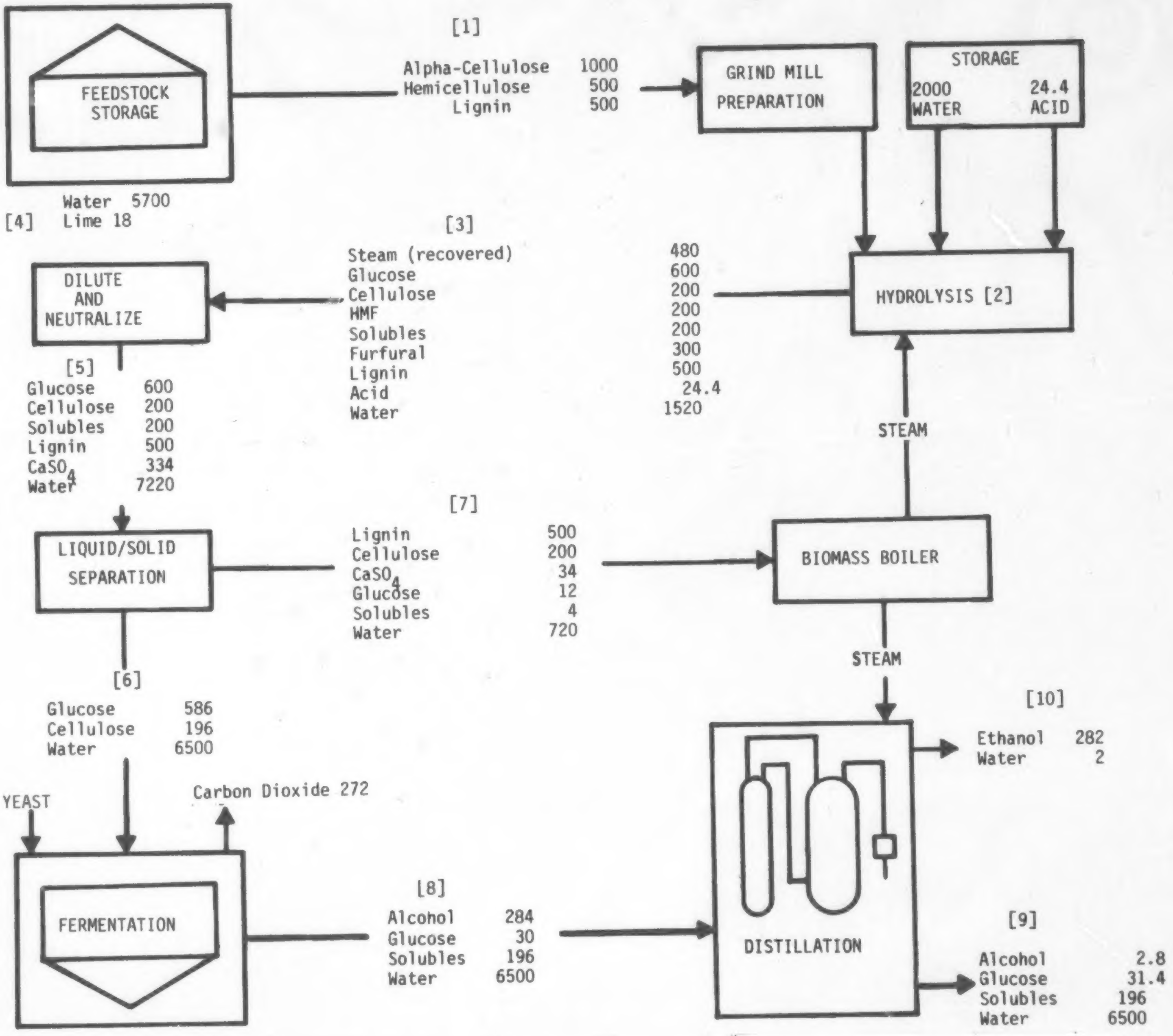
FEEDSTOCK STORAGE
[1]
Alpha-Cellulose 1000
Hemicellulose 500
Lignin 500
GRIND MILL PREPARATION
STORAGE
2000 WATER
24.4 ACID
[4]
Water 5700
Lime 18
[3]
Steam (recovered) 480
Glucose 600
Cellulose 200
HMF 200
Solubles 200
Furfural 300
Lignin 500
Acid 24.4
Water 1520
HYDROLYSIS [2]
DILUTE AND NEUTRALIZE
[5]
Glucose 600
Cellulose 200
Solubles 200
Lignin 500
CaSO4 334
Water 7220
STEAM
LIQUID/SOLID SEPARATION
[7]
Lignin 500
Cellulose 200
CaSO4 34
Glucose 12
Solubles 4
Water 720
BIOMASS BOILER
STEAM
[6]
Glucose 586
Cellulose 196
Water 6500
[10]
Ethanol 282
Water 2
YEAST
Carbon Dioxide 272
FERMENTATION
[8]
Alcohol 284
Glucose 30
Solubles 196
Water 6500
DISTILLATION
[9]
Alcohol 2.8
Glucose 31.4
Solubles 196
Water 6500

FIGURE 34: Material Balance (tons per day)

TABLE 8

MATERIAL BALANCE

STREAM	WEIGHT PERCENT	TONS PER DAY	
1) Feed into Extruder			
alpha-cellulose	24.8	1000	
hemicellulose	12.4	500	
lignin	12.4	500	
water	49.8	2000	480,192 gals.
acid (98%)	0.6	24.4	
TOTAL	100.0	4024.4	
2) Reaction Zone			
glucose	14.9	600	
unreacted cellulose	9.9	400	
hemicellulose decomposition product	12.4	500	
lignin	12.4	500	
acid	0.6	24.4	
water	49.8	2000	
TOTAL	100.0	4024.4	
3) Discharge from extruder			
glucose	14.9	600	
unreacted cellulose	5.0	200	
hydroxymethyl furfural	5.0	200	
solubles	5.0	200	14.9% glucose mud
furfural	7.5	300	
lignin	12.4	500	
acid	0.6	24.4	
water	37.7	1520	
steam (flashed)	11.9	480	
TOTAL	100.0	4024.4	

Table 8 (Cont'd)

		Weight Percent	Tons Per Day	
4) Neutralizing lime			18	
5) From neutralization tank				
glucose		6.8	100	
unreacted cellulose		2.3	200	1,368,000 gals used
solubles		2.3	200	for spray washing
lignin		5.7	500	
$CaSo_4$		0.4	34	
water		82.5	7220	
	TOTAL	100.0	8754	
6) Liquid stream from centrifuge				
glucose		8.0	586	
unreacted cellulose		2.7	196	8/0% sugar solution
water		89.3	6500	
	TOTAL	100.0	7283	
7) Centrifuge cake				
lignin		34.0	500	
unreacted cellulose		13.6	200	
$CaSo_4$		2.3	34	49% moisture boiler fuel
glucose		0.8	12	
solubles		0.4	4	
water		48.9	720	
	TOTAL	100.0	1470	
8) From fermenter				
alcohol		3.9	284	
unfermented sugars		0.4	30	
solubles		2.7	196	3.9% beer
water		89.3	6500	
carbon dioxide		3.7	272	
	TOTAL	100.0	7282	

Table 8 (Cont'd)

		Weight Percent	Tons Per Day	
9) Still bottoms				
alcohol		0.04	2.8	
glucose		0.4	31.4	
solubles		2.9	196	
water		96.6	6500	
	TOTAL	100.0	6730.2	
10) Alcohol product				
ethyl alcohol		99.3	282	85,584 gallons per day
water		0.7	2	
	TOTAL	100.0	284	

TABLE 9

PARTICULATE AND GASEOUS EMISSIONS FOR DIRECT COMBUSTION OF BIOMASS RESIDUES COMPARED WITH COAL COMBUSTION

Kg/10^6 BTU

PARAMETER	MSW[a/]	WOOD RESIDUE[b/]	BAGASSE[c/]	COAL[d/]
Particulates	0.04-0.8	0.6	1.1	0.04
SO_x	0.1	0.06	0	0.5
NO_x	0.2	0.04	0.1	0.3
CO	0.04	1.2	0.1	0.04
HC	---	1.4	0.1	0.02

[a/] Assumes 6,000 BTU/lb heating value

[b/] Assumes 6,000 BTU/lb heating value

[c/] Assumes 4,600 BTU/lb heating value

[d/] Assumes bituminous coal, 3% sulfur content, 15% ash, 12,000 BTU/lb heating value change the volume of wastewater to be treated. The BOD load will be high, but again amenable to conventional wastewater treatment techniques.

TABLE 10. COMPOSITION OF STILLAGE

COMPONENT	WEIGHT % (DRY BASIS)
Mineral matter	28.5 - 29.0
Sugars	10.0 - 12.0
Proteins	8.0 - 10.0
Volatile acids	1.0 - 2.0
Gums	20.0 - 22.0
Combined lactic acid	4.0 - 7.0
Other combined organic acids	1.0 - 2.0
Glycerol	5.0 - 6.0
Wax, Phenolics, Lignins, etc.	12.0 - 22.0

SECTION 8

ECONOMICS

A. SCALE-UP TO INDUSTRIAL FACILITY

At the NYU Westbury pilot plant, which handles nominally 1 ton per day (dry basis) of cellulosic feedstock, research continues on optimizing many aspects of the process and on processing a selection of additional feedstocks. However, it is felt that results to date have been sufficiently promising to justify scaling-up to a "demonstration" plant of some 100 tons per day capacity. A full-scale commercial facility would be the next step, and some details follow from studies by NYU, the Werner & Pfleiderer Corporation, who possess extensive experience in scaling-up of extruder operations, and a complete engineering feasibility study, carried out by Vulcan Cincinnati, Inc., (54) of a full-scale plant producing 25 million gallons per year of alcohol.

Process details are as follows: It will have an 1875 ton per day (dry basis) throughput of sawdust or wood chips, reduced if necessary to ¼" by hogmill, hydrolyzing with 1.5% sulfuric acid at 450 F and 500 psi in a Werner & Pfleiderer co-rotating twin-screw extruder. The product is discharged into a flash chamber at 100 psi, from which steam and volatiles such as furfural are conveyed to a recovery system and the glucose mud at pH about 1 is pumped to a mixing tank where it is adjusted to pH 4.5 with 10% lime slurry.

After centrifuging, the solids cake at 45% moisture is conveyed to the boiler, while the centrifugate at 8% glucose is delivered to the fermenter; fermentation is done batchwise on a 36-hour cycle with yeast recycle and the product distilled to give the azeotrope, 190 proof alcohol. The dried stillage will be used as boiler fuel until a market is developed for it as animal feed. The azeotrope is dehydrated to 198+ proof with ether, then denatured with 5% unleaded gasoline according to the CDA-20 formula for use as fuel alcohol.

A 60% cellulose conversion is assumed, together with measured or typical values for separation and fermentation efficiencies. A 91% capacity factor is taken and 24 months for design and construction once financing is arranged; suitable sites have been selected for the facility with ample feedstock available at $15 per ton. Inflation is allowed at 12% per year, and overall the yield of ethanol is 45.9 gallons per ton.

A commercially viable plant needs to be on a fairly large scale because of the capital-intensive nature of the acid hydrolysis process. It is desirable to employ co-generation of heat and electrical energy, and these factors are combined with others as discussed in the next subsection when the decisions on scale are made. In the Vulcan feasibility study, a specific site for the plant is detailed, the most important features being proximity to a source of cellulosic raw material, a supply of process water, and transport facilities; further to this, possible alternative sites have been identified and described.

B. INVESTMENT COSTS AND RETURN ON INVESTMENT

Table 11, from Rugg (52), gives a capital cost summary for an 1800 ton per day plant, and Table 12 shows the make-up of the cost of production. Table 13 gives the details of the return on investment, and Figure 35 is a sensitivity analysis for this. Clearly, these economic projections will need to be updated at the time of evaluating a commercial operation, but the relative costs and sensitivities will undergo little change. Raw material costs are of major significance. The range is from $30 per ton, which is possibly the maximum for economic conversion into glucose, to zero: municipal waste as a feedstock may even have a negative cost, but some kind of separation step required would raise this to zero or slightly above. This is discussed further in the next subsection.

By-product credits are of course very dependent on market conditions, but can make such a significant difference to the overall economics of the process that they must be considered. Carbon dioxide by-product is shown as an option in the tables. Lignin by-product possibilities are discussed in the lignin utilization subsection. Sale of electricity as a by-product at 6¢ per kilowatt-hour would add a substantial offset to the ethanol price: Table 14 from a recent calculation shows this effect, together with that of variation in the feedstock cost.

Further points to be noted from the sensitivity analysis are the small effect of equipment cost, and the marginal improvement in ROI if conversion yields are pushed above 60%, due to the decreased credit for sale of the electricity by-product.

Costs are given here for both single- and two-stage processes, and as mentioned in the section on maximum use of feedstock, it appears at this time that the two-stage process would have higher costs which are not compensated by the higher yield. Overall, the assumptions and projections in this economic analysis are conservative, and thus the projection of costs and benefits should be realistic, clearly justifying further investment in scaling-up the NYU process.

C. MUNICIPAL SOLID WASTE AS FEEDSTOCK

It is widely recognized that large quantities of cellulose are present as a renewable resource in MSW, principally in the form of vegetable and paper waste. However, the difficulties in utilizing this resource are not quite so widely appreciated. Most recovery operations in use on MSW burn the waste first, then extract useful materials from the residue. Processes designed to extract resources before combustion have met with severe practical difficulties, a case in point being the Hempstead Resources Recovery Corporation (Westbury, NY). This essentially involves a "giant blender" treatment

TABLE 11: CAPITAL COSTS

	Installed Cost (million $)	
	Single-Stage[a]	Two-Stage[b]
Materials Handling and Hydrolysis		
Bulk unloading and storage for wood	1.8	1.8
Sawdust handling, grinding and feeding	1.2	1.2
Acid unloading, storage and feeding (two-stage = (63/0.7) × one-stage = 1.374 × one-stage)	1.0	1.4
Water metering	0.2	0.2
Extruder reactors	17.5	17.5
Prehydrolysis reactors		6.5
Engineering	2.0	2.7
Installation of extruders	1.8	2.4
Installation of rest of system	2.5	3.4
Subtotal	28.0	37.1
Separation and Continuous Fermentation	6.4	6.9
Distillation	9.0	9.6
Piping, Refrigeration, Steam and Controls	6.4	6.9
CO_2 Recovery Plant	6.0	6.3
Total Inside Battery Limits	55.8	66.8
Outside Battery Limits	25.6	27.5
Total (site, building, cooling tower, waste disposal/cleanup, etc.)	81.4	94.3

[a] Fuel-grade alcohol produced: 142.7 million liter/yr. CO_2 by-product produced: 90,700 metric ton/yr.

[b] Fuel-grade alcohol produced 159 million liter/yr. CO_2 by-product produced: 94.4 million metric ton/yr.

TABLE 12: PRODUCTION COSTS

	Single-Stage[a]		Two-Stage[b]	
	Without CO_2	With CO_2	Without CO_2	With CO_2
Inside Battery Limits	49.8	55.8	60.5	66.8
Outside Battery Limits	25.6	25.6	27.5	27.5
Post-tax Return – With CO_2				
1.427×10^8 liter/yr × (42.3 − 25.2) × 55%		13.42		
1.59×10^8 liter/yr × (42.3 − 28.3) × 55%				12.24
Tax credit for depreciation				
[(55.8 million × 10%/yr) + (25.6 million × 2%/yr)] × 45% tax		2.74		
[(66.8 million × 10%/yr) + (27.5 million × 2%/yr)] × 45% tax				3.25
Investment tax credit spread over 10 years				
(10% × 81.4)/10		0.81		
(10% × 94.3)/10				0.94
Total return		16.97/yr		16.43/yr
Post-tax Return – Without CO_2				
142.7 million liter/yr × (42.3 − 28.8) × 55%	10.58			
142.7 million liter/yr × (42.3 − 31.5) × 55%			9.47	
Tax credit for depreciation				
[(49.8 million × 10%/yr) + (25.6 million × 2%/yr)] × 45%	2.47			
[(60.5 million × 10%/yr) + (27.5 million × 2%/yr)] × 45%			2.97	
Investment tax credit spread over 10 years				
(10% × 75.4 million)/10	0.75			
(10% × 88.0 million)/10			0.88	
Total return	13.80/yr		13.32/yr	

[a] Alcohol production, 142.7 million liter/yr.
[b] Alcohol production, 159 million liter/yr.

TABLE 13: RETURN ON INVESTMENT

	\$/metric ton Sawdust		¢/l Ethanol	
	Single-Stage	**Two-Stage**	**Single-Stage**	**Two-Stage**
Raw Material Costs				
Sawdust: \$16.53/metric ton delivered wet, 50% H_2O	33.06	33.06	14.01	12.55
Acid: 98% H_2SO_4 at \$66.12/metric ton[b]	0.80	1.61	0.34	0.61
Neutralizing Agent: $Ca(OH)_2$ at \$33.06/metric ton[c]	0.25	0.51	0.11	0.19
Total Raw Material Costs	34.11	35.18	14.46	13.35
Operating Costs – Labor and Maintenance				
Labor – Single-Stage: 30 operators, 7/shift at \$21,000; 6 foreman at \$24,000; 1 supervisor at \$28,000 = \$802,000/yr	1.32		0.56	
Labor – Two-Stage: 35 operators, 6/shift at \$21,000; 6 foremen at \$24,000; 1 supervisor at \$28,000 = \$907,000/yr		1.50		0.57
Maintenance: material and labor at 6% of inside battery limits (see Table IV) one-stage, \$55.8 million = \$3.348 million/yr; two-stage, \$66.8 million = \$4.008 million/yr	5.53	6.63	2.34	2.52
Total Labor and Maintenance Costs	6.85	8.13	2.90	3.09
Operating Costs – Energy				
Hydrolysis: electricity at 4¢/kWh steam generated from lignin	9.92	17.63	4.20	6.69
Fermentation: electricity at 4¢/kWh	1.22	1.32	0.52	0.50
cooling water at 5¢/3785 liters	0.13	0.13	0.06	0.05
Distillation: electricity at 4¢/kWh	0.10	0.11	0.04	0.04
steam at \$4/454 kg	7.45	11.30	3.16	4.29
cooling water at 5¢/3785 liters	0.88	0.97	0.37	0.38
Total Energy Costs	19.70	31.46	8.35	11.95
Total Operating Costs	26.55	39.59	11.25	15.04
Overhead Costs				
Direct Overhead: 40% of labor & supervision (single-stage, \$802,000 × 0.40 = \$321,000/yr; two-stage, \$907,000 × 0.40 = \$363,000/yr)	0.53	0.60	0.22	0.23
General Plant Overhead: 65% of labor, supervision & maintenance (single-stage, \$4.150 million × 0.65 = \$2.698 million/yr; two-stage, \$4.915 million × 0.65 = \$3.195 million/yr)	4.46	5.29	1.89	2.01
Insurance and Property Taxes: 1.5% of total investment (single-stage, \$81.4 million × 0.015 = \$1.221 million/yr; two-stage, \$94.3 million × 0.015 = \$1.415 million/yr)	2.02	2.34	0.85	0.89
Total Overhead Costs	7.01	8.23	2.96	3.13
Total Manufacturing Cost	67.67	82.99	28.67	31.51
By-Product Credit: CO_2 at 5.5¢/kg	– 8.19	– 8.65	– 3.47	– 3.28
Total Adjusted Manufacturing Cost	59.48	74.34	25.20	28.23

[a] Plant summary and conversion factors. *One-stage:* production, 142.7 million liter/yr of fuel-grade ethanol, plus 90,700 metric ton/yr of CO_2 by-product; conversion, 60% κ-cellulose to glucose, 58% hemicellulose to sugars. *Two-stage:* production, 159 million liter/yr of fuel-grade ethanol, plus 93,400 metric ton/yr of CO_2 by-product; conversion, 80% hemicellulose to sugars; no CO_2 from pentose. *Both:* throughput, 1814 metric ton/day (604,062 metric ton/yr) of sawdust; conversion, 98% recovery of sugars, 8.6% glucose solution, 45% glucose to ethanol, 30% pentose to ethanol, 43% glucose to CO_2; capacity scaling factor, $(63/57)^{0.7} = 1.072$.

[b] 1.22 and 2.44% of sawdust dry weight for single- and two-stages, respectively.

[c] 1.24 and 2.48% of sawdust dry weight for single- and two-stages, respectively.

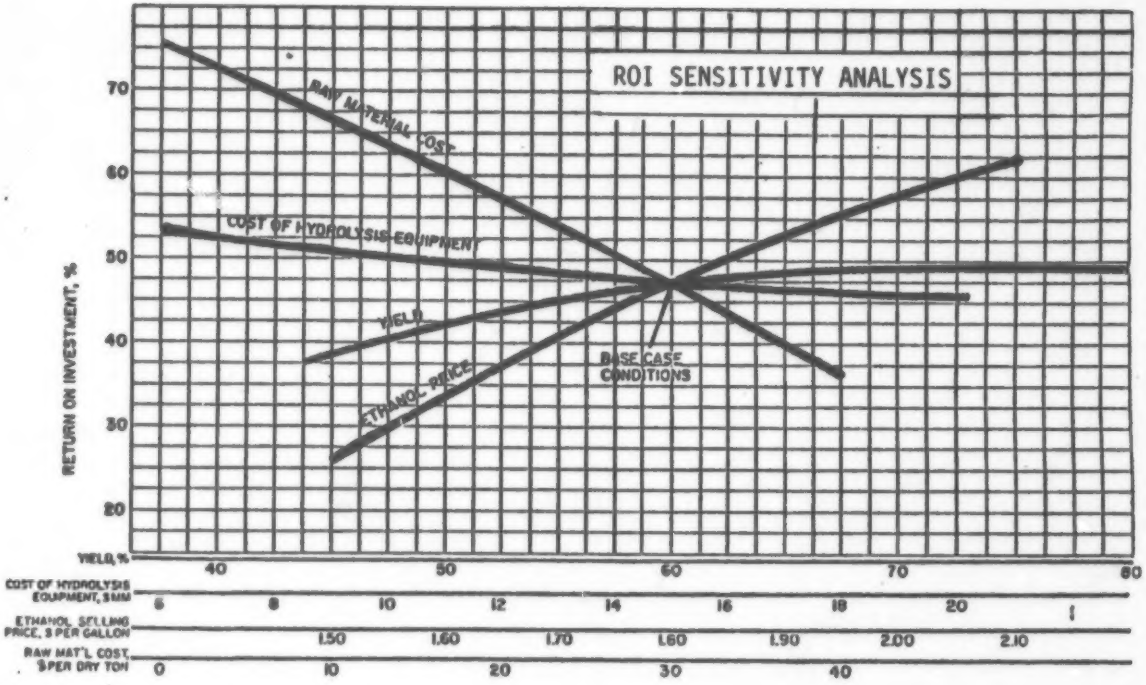

FIGURE 35: ROI Sensitivity Analysis

TABLE 14. EFFECT OF FEEDSTOCK COST AND ELECTRICITY SALE

RAW MATERIAL COSTS	¢/GALLON ETHANOL	¢/LITER ETHANOL
Cellulosic Raw Material (@ 0 → $30 per ton)	0 → 66.0	0 → 17.4
Other Raw Materials (Acid, Lime, Nutrients, etc.)	6.6	1.7
OPERATING COSTS		
Labor	7.6	2.0
Maintenance	15.2	4.0
Energy	0.0*	0.0*
OVERHEAD COSTS		
Direct Overhead	3.0	0.8
General Plant Overhead	11.8	3.1
Insurance and Property Taxes	6.3	1.7
SUBTOTAL	50.5 → 116.6	13.3 → 30.8
*BYPRODUCT CREDIT		
Electricity @ 6¢ per kWH	82.05	21.7
TOTAL	-31.6 → 34.6	-8.3 → 9.1

with a Black-Clawson Hydrapulper, followed by various separation operations, leaving the cellulosic portion as a papier-mâché-like material at 50% moisture. Used as boiler fuel, the material would power the plant itself and supply electricity for half the Town of Hempstead, at the rate of 40 MW. Arrangements were made to test some of this cellulosic material as a feedstock for the NYU hydrolysis process, it being anticipated that "extraneous" components such as glass and plastics not already recovered from it would be inert as far as the extruder reactions are concerned. Unfortunately, before the material could be supplied to NYU for the tests, the HRRC plant was forced to suspend operations because of unallowable levels of contaminants in its boiler emissions. However, it is intended to investigate at some future date the hydrolysis of MSW in some suitable form in the NYU extruder. Certainly a feedstock which is already collected and has such a low cost should not be left unchecked.

SECTION 9

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APPENDIX A

INITIAL EXTRUDER TRIALS AT WERNER & PFLEIDERER CORP.

Some extracts are given from tests carried out in November, 1976, at Waldwick, NJ, by personnel from NYU, EPA, and WPC. A model ZSK-53V extruder was used, with waste paper pulp as the feedstock.

FEEDING

Waste paper slurry as supplied contained approx. 92% water. When stirring it, the consistency indicated that delivery with Moyno pump would be possible. However, when trying this approach, the paper slurry does not readily flow through the inlet of the Moyno pump. Only the ZDS-D twin-screw feeder with agitators worked reasonably well. The delivery rate fluctuated somewhat due to change in water content of the slurry when exposing slurry to squeezing during delivery. As a result of these feeding problems, material could not be preheated as initially thought but it was fed cold.

PROCESSING

Due to the low slurry concentration, mechanical squeezing of water and increasing solids concentration was intended. As it turned out, this approach did not work well. The restriction in the form of left-handed screw or kneading elements resulted in total pluggage with compacted paper and water as well as slurry was forced back through the rear barrel opening. It is advisable to start initially with higher concentration, concentrating the slurry by some other means.

Conveying efficiency of this slurry is affected by the screw configuration and amount of water present. When forming to strong seal downstream, the slurry concentration in feed upstream is reduced resulting in poorer conveyance. Subsequently, material floods the feed port. Using existing screw elements, only change in pitch could be tolerated as a seal. Screws 1, 2, and 4 led to that conclusion. The elements with more positive conveying action in the feed zone should be explored.

When material is conveyed in the machine, the heating of slurry was done by external electrical heaters. At the throughputs of 100 lbs/hr or less, this solution is adequate. However, if higher rates would be explored (assuming no feed problems and same concentration) this heating might not be adequate.

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DISCHARGE

Initially it was intended to discharge the material through 8-0 transition and 2" pipe into a series of expansion drums to condense the generated steam. However, the material could not be transported under this arrangement due to compacting of paper at the end of the screw. This resulted in pluggage. Therefore, an open discharge was made. For safety reasons, the discharge was through the opening of the vent barrel turned upside down. For any further work, a direct flanging of the machine to the expansion tank should be explored. During the test, paper balls were discharged together with steam to the atmospheric pressure.

ACID INJECTION

Sulfuric acid was injected via triplex pump downstream into a steam/paper slurry at approx. 400 F. The reaction was supposed to be taking place resulting in syrup-like consistency of material. Due to open discharge no high pressure could be maintained in order to assure the reaction. Therefore, no conversion of cellulose to glucose was determined in the discharged material. However, there is no reason to believe that conversion would not take place if expansion chamber could be flanged to the machine and pressurized.

CONCLUSIONS

The feasibility of the process was demonstrated successfully. There are some sections of the process which need improvement:

1. Pumping of the slurry.
2. Feed intake.
3. Pressure seal.
4. Discharge into expansion chamber.

APPENDIX B

MOBILE HYDROLYSIS UNIT PROPOSAL

Some details follow from a preliminary proposal by W. Brenner and B. Rugg, Dept. of Applied Science, New York University, July 1979, entitled "Development of Mobile Acid Hydrolysis Unit for Production of Fermentable Sugars from Agricultural, Forestry, and Selected Industrial Residues to make Ethyl Alcohol Automotive Fuels".

Development of a mobile acid hydrolysis unit for field demonstration of the technical and economic viability of the NYU process is proposed in order to implement the non-petrochemical production of ethyl alcohol, especially for automotive fuel use. The sugar products obtained will be fermented to alcohol in a local or regional facility. This mobile acid hydrolysis demonstration unit will provide maximum flexibility for utilizing local sources of potential residues, including paper wastes. The feedstocks for its operation will, moreover, be variable and optimized depending on local and seasonal availability factors and costs. Locations for field demonstrations will be selected by the contracting agency.

Mobility of the unit will assure that various local farm, forestry, and other resources can be evaluated as feedstocks for alcohol production when available seasonally. Also, substantial transportation expenses can be saved by shipping a small quantity of a high value, higher density sugar concentrate to an alcohol fermentation plant, rather than a larger volume of low-valued, low bulk density agricultural or other residues, to serve as feedstocks for a central acid hydrolysis/fermentation plant complex. Furthermore, all unreacted material from the acid hydrolysis unit will be usable in place as a fertilizer supplement, etc., instead of becoming a disposal problem at such a central acid hydrolysis/fermentation plant. Where local conditions indicate, the mobile acid hydrolysis demonstration can, of course, be used as a stationary facility in conjunction with an alcohol fermentation plant.

This mobile acid hydrolysis demonstration unit will be based on a Werner & Pfleiderer Company ZDS-K83 twin screw reactor for the acid hydrolysis of the cellulosic feedstocks. Power and other utility needs for its operation will be supplied by a Caterpillar Model 3306 generator with a 96 gallon fuel tank or equivalent, and a Hydrosteam Model 1652 boiler. Ancillary equipment will comprise a McMaster & Carr screw conveyor system, a crammer/feeder, acid pumps, a discharge mechanism, and collection tanks. The unit will also feature the appropriate instrumentation for operation and control of the ZDS-K83 acid hydrolysis reactor, basic analytical equipment, ventilation,

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plumbing, electrical connections, etc.

Table B-1 outlines the major components and provides a rough estimate of their cost. This mobile acid hydrolysis demonstration unit will be mounted on two International Model 1600 Loadster trucks with custom bodies. One truck will carry the ZDS-K83 acid hydrolysis reactor with feed, discharge, and collection equipment. The generator, boiler, acid pumps, and various other necessary equipment will be mounted on the other truck. Such a mobile unit will be able to accept a wide range of agricultural, forestry, and selected industrial products and their residues, and convert them to fermentable sugars with yields in excess of 50% based on the available cellulose with reaction times on the order of only 10 seconds.

The following time schedule based on a 1½ year period of demonstrations is proposed for development and field demonstration; some of the activities will naturally be carried out concurrently.

1.	Specification and ordering of equipment	2 months
2.	Delivery of equipment	6 months
3.	Installation of equipment	3 months
4.	Shakedown and testing	4 months
5.	Field demonstration	18 months
6.	Evaluation of results	3 months

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TABLE B-1

MOBILE ACID HYDROLYSIS UNIT
BASED ON WPC ZDS-K83

	Item/Description	Weight/Dimensions/Power Required	Approx. Cost
1.	2 Trucks International Mod. 1600 Loadstar with custom body	20 feet, custom body	$40,000
2.	ZDS-K83 Extruder in stainless with control panel and Crammer feeder	8000 lbs., 17.5 feet long 75 kW at 480V - 3 phase	300,000
3.	Instrumentation: recorders and Dynisco combined temp/pressure transducer and indicator TPT- and DR-482		3,000
4.	Generator, 96 gal fuel tank Caterpillar Mod. 3306	4700 lbs., 150 kW at 480V - 3 phase	20,000
5.	Boiler - 245 lbs/hr Hydrosteam Mod. 1652	750 lbs., 72kW at 480V - 3 phase	15,000
6.	Acid injection pump - stainless Pennwalt	500 lbs.	3,500
7.	Kamyr Ball Valve and hydraulics**	1000 lbs.	4,500
8.	Collection Equipment	500 lbs.	1,000
9.	Handling Equipment	750 lbs.	1,500
10.	Ventilation Equipment	500 lbs.	1,000
11.	Analytical Equipment	500 lbs.	15,000
12.	Plumbing/Electrical	1,000 lbs.	5,000
13.	Safety Equipment	--	1,500
	TOTAL	18,700 lbs. = 9½ tons	$411,000

TOTAL ESTIMATED PROJECT COST FOR THREE YEAR PERIOD = $1.5 to $2 million

**An updated design for a mobile unit would, of course, replace these items by a fully continuous discharge along the lines of the orifice system described in Section 4B.

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APPENDIX C

SOLAR STEAM GENERATION PROPOSAL

With the aim of further reducing the use of electrical energy for the NYU pilot plant, a study was done on the possibility of using a solar concentrator to generate some of the energy required. At present, (i) steam is injected into the reaction zone at 500 F, (ii) the extruder barrel is heated electrically to 500 F, and (iii) the feedstock pulp is preheated in the crammer feeder by passing steam through its jacket. It is proposed to use a heat transfer oil such as Dowtherm-A, rated to 750 F, as the operating fluid. Although expensive ($6/gal), it is preferred since considerable problems have been encountered by other investigators working with water, due mainly to the corrosion properties and high vapor pressure of water at these temperatures. The hot oil would be circulated through heating pipes in the boiler, supplementing the electrical heat, and also through the jacket of the extruder barrel (at present this jacket is not in use), again to supplement the electrical heat.

A degree of flexibility would be included in the system, so that on days of lower insolation, when the lower-temperature heat produced is of no use for process steam and process heat, it could be used to pre-heat the feedstock pulp and boiler feedwater; this would be done by passing oil through the crammer jacket in place of steam, and through a shell-and-tube heat exchanger for the boiler feedwater.

A parabolic-dish concentrator would easily achieve high temperatures, but largely because of the sun-tracking requirement, is expensive. An Omnium-G, for example, with an 18 ft diameter dish producing some 25 kW, as 70 lb/hr of steam at 1100 F, would cost $31,000. A typical parabolic-trough concentrator, for instance Suntec, with a 9 ft aperture (i.e. collecting width) for 20 lb/hr of steam at 600 F would need to have a collecting area of around 360 sq ft, and thus a length of 40 ft, or 2 modules; the price of this is $14,000 for the concentrator plus $5000 for the controls, a total of $19,000. However, a maximum temperature of 600 F would be expected, whereas 700 F would be preferable for heat transfer in the boiler. On the other hand, existing solar installations are operated at somewhat lower temperatures for industrial process heat or steam.

To generate steam with solar energy for the NYU process would require not just adapting existing commercial equipment to the new process, but development of technology new in itself; in particular, components such as flexible couplings for piping to the movable concentrator would need to be developed to handle the high temperatures and pressures encountered. Thus, solar generation of steam for the pilot plant would constitute a sizable

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research project on its own, and under the circumstances, it was decided after carrying out extensive calculations to defer further action.

APPENDIX D

NYU BENCH-SCALE FERMENTATION TRIALS

For these trials, commenced but not completed during this contract period, the aim was to demonstrate the fermentability of the product from the NYU continuous cellulose hydrolysis, and to establish baseline conditions for the fermentation. It was decided to proceed straight to a bench-scale operation, rather than begin with test-tube trials, and a New Brunswick 2-liter laboratory fermentor was set up. This has provision for stirring, heating and cooling, aeration, and sampling, as well as illumination, which was not used here. An added capability was provided by the use of a Kaye Digistrip II Datalogger; it was programmed to sound alarms for unacceptable deviations from the selected conditions, as well as giving a readily visible display and printed periodical log of these conditions. Additionally, the datalogger was set to control the conditions for a separate experimental set-up for yeast growth (aerobic, as opposed to the anaerobic process of fermentation.)

YEAST

A variety of yeast was selected which already has most of the characteristics desired, namely Saccharomyces cerevisiae var. Carlsbergensis. This is a brewers' bottom-fermenting ale yeast; it is vigorous in solutions having sugar strength around the desired 7% and is tolerant of many "foreign" substances; its bottom-fermenting characteristic reduces any tendency to foam; and it has no need for a high alcohol tolerance (high, that is, by winemaker's standards.)

SUBSTRATE PREPARATION

Substrates for fermentation were prepared by centrifuging the extruder product as described in the section on "Separation", then combining the glucose-rich liquid fractions from runs with the same feedstock and reaction conditions. This centrifugate was then adjusted to pH about 5 with calcium carbonate (powdered form), filtered through activated charcoal, and stored under refrigeration.

FERMENTATION PROCEDURE

A sample for a run was placed in the glass fermentor vessel together with appropriate nutrients (potassium phosphate and urea) and equilibrated, at which point the yeast was added and the first set of measurements were taken. Progress of the fermentation was followed by monitoring several

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quantities as follows. Consumption of glucose and production of ethanol and carbon dioxide cause a considerable decrease in the density of the mixture. This was followed by taking readings on standard hydrometers; a set was obtained, calibrated on the Brix scale (% sugar by weight), with each one covering part of the required density range very accurately. An extra hydrometer, calibrated for specific gravity and potential alcohol as well, covered the whole range with somewhat less precision, and was used as a check. All measurements were taken on aliquots extracted from the fermentor and equilibrated in a thermostatted bath. Alcohol content was estimated with a vinometer (essentially a capillary measurement of surface tension, as used by vintners). Acidity was checked with a pH meter.

ACCLIMATION PROCEDURE

A method for acclimating the yeast to the hydrolyzate was devised and is as follows. For the first stage, the yeast was given pure glucose ("dextrose", made up to 7% by weight) and nutrients; this served as a control. After fermentation ceased, the yeast was transferred for use in the next stage, and in this procedure a mechanical loss of some 10% was compensated by a natural increase, thus leaving about the same quantity. In the second stage, the mixture was made up with some of the hydrolyzate included: total glucose was kept at the same 7%, but in this case made up 90% from pure dextrose and 10% from glucose in the hydrolyzate. Nutrients were the same, as were conditions except where noted. In successive stages, the transfer procedure was repeated and the proportion of the hydrolyzate incremented by 10% steps until 100% hydrolyzate was reached. At this point, sugar utilization and fermentation times were still good, so the same yeast strain was used for further experiments, namely (i) yeast growth, and (ii) fermentation of white pine hydrolyzate.

RESULTS

Table D-1 and Figure D-1 summarize the experiments. It may be noted that in the early stages of setting up the bench-top fermentation system, changes were made in the temperature, the rapid fermentation at 35 C being abandoned in favor of the lower alcohol loss at 25 C.

Most importantly, the conclusion may be drawn that the product from the NYU cellulose process is fermentable. The aim of these trials was simply to demonstrate fermentability, so it would be expected that further improvement and optimization of the fermentation process could now easily be undertaken.

TABLE D-1

FERMENTATION OF NEW YORK UNIVERSITY HYDROLYZATE

(Aspen Sawdust, Saccharomyces cerevisiae var Carlsbergensis Yeast)

RUN NUMBER	TEMPERATURE °C	TOTAL GLUCOSE	FRACTION FROM HYDROLYZATE	TIME TO HALF GLUCOSE CONSUMPTION	FRACTION OF GLUCOSE CONSUMED	YEAST TRANSFER NO.
F-4	35	10% (w/w)	0%	33 hrs.		
F-7	35	7%	10%	33 "	-	
F-8	30	↓	20%	16 "	-	1
F-9	30		30%	13 "	-	2
F-10	27		40%	14.5 "	-	3
F-11	22		50%	24.5 "	-	4
F-12	25		60	21 "	-	5
F-13	25		"	25 "	98.0%	6
F-14	25		70%	26 "	98.7%	7
F-15	25		"	25 "	96.5%	8
F-16	25		80%	26 "	97.3%	9
F-17	25		"	25 "	98.2%	10
F-18	25		90%	28 "	99.0%	11
F-19	25		100%	30 "	98.6%	12
F-20	25		100%	28 "	99.0%	13

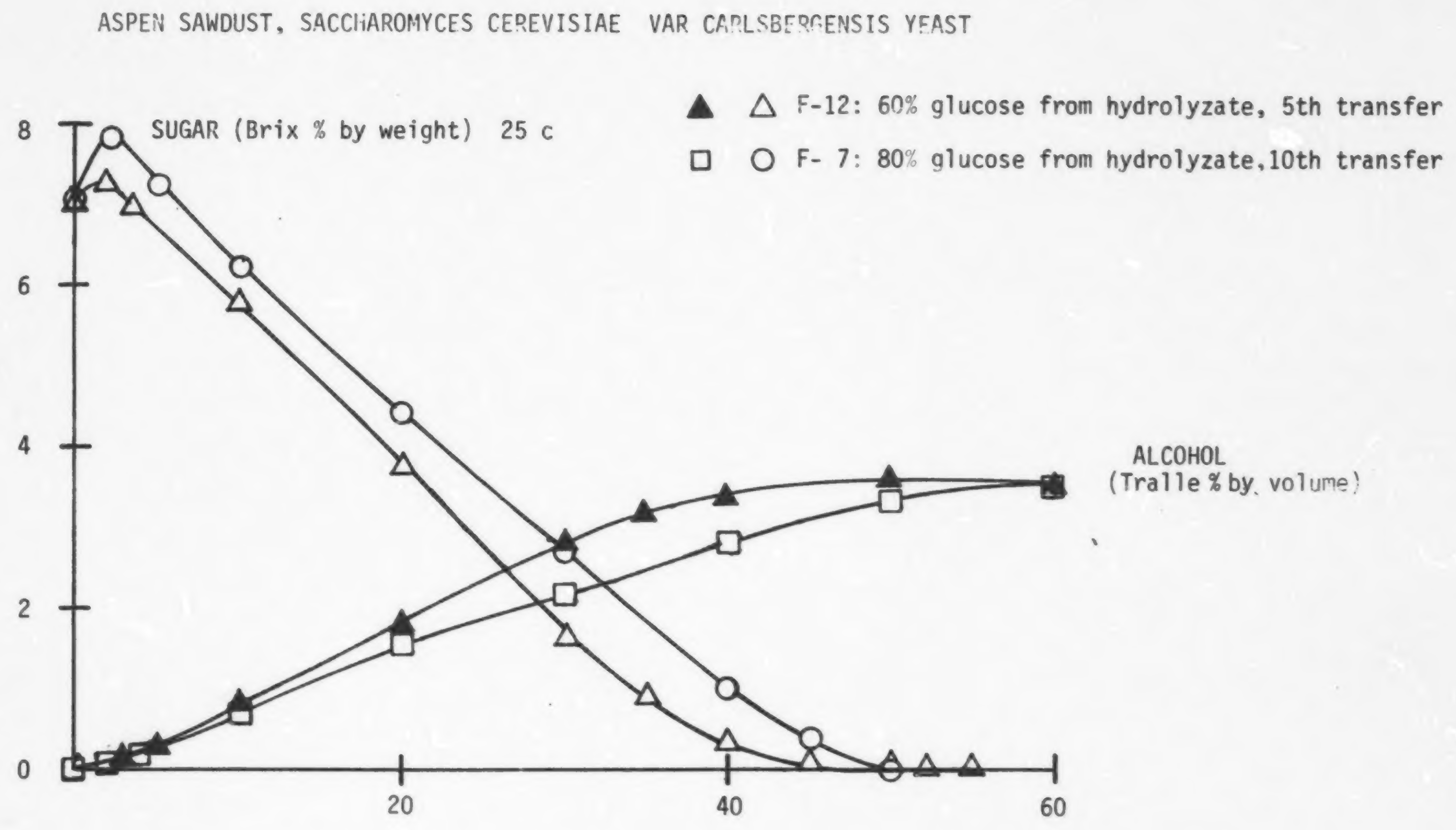

FIGURE D-1: Fermentation of Aspen Hydrolyzate

APPENDIX E

UNIVERSITY OF GEORGIA BIOCONVERSION TRIALS

Investigations have been made in the Department of Biochemistry, under the direction of Prof. L.G. Ljungdahl, on the behavior of high-temperature bacteria. One genus they have described for the first time: *Thermoanaerobacter ethanolicus* is an extreme thermophilic (i.e., growing over 70 C), non-sporogenic, anaerobic bacterium isolated from alkaline and slightly acidic hot springs located in Yellowstone National Park. It is capable of fermenting glucose and/or cellobiose, giving ethanol and carbon dioxide as the main products (thus the overall action is similar to that of a *Saccharomyces* yeast).

Another thermophilic anaerobic bacterium, *Clostridium thermocellum*, is also under study, and it is capable of hydrolyzing cellulose to oligosaccharides, cellobiose, and glucose; it can also ferment these sugars to lactate, acetate, ethanol, carbon dioxide, and hydrogen.

In nature, these two are members of a whole group of anaerobic bacteria which break down cellulosic biomass ultimately to carbon dioxide and methane. It is observed that they operate synergistically, by supplying substrates, removing inhibitory products, and presumably also by contributing nutrients and cofactors.

In the laboratory, *T. ethanolicus* and *C. thermocellum* have been grown both separately and in mixed cultures on cellulosic materials and various carbohydrates. Mixed cultures give both higher conversion yields and higher rates, presumably because *T. ethanolicus* removes xylose and cellubiose, which inhibit *C. thermocellum*. It is found that hydrolyzate from the NYU process gives results similar to those for steam-exploded wood material when subjected to such a mixed bacterial culture; thus, this is a promising avenue for investigation in downstream processing of the NYU product.

APPENDIX F

LOUISIANA STATE UNIVERSITY BIOCONVERSION TRIALS

Investigations were carried out in the Department of Microbiology, under the direction of Dr. V.R. Srinivasan, on a subcontract from NYU, principally on (i) yeast growth on acid hydrolyzate, and (ii) bacterial conversion of acid hydrolyzate to methane.

Experiments with a strain of Saccharomyces cerevisiae measured the harvested yeast cell weight after growth for 72 hours at 30 C. Pure glucose as substrate was compared with hydrolyzate samples from the NYU process after charcoal filtration; results indicated that yeast production, relative to the amount of carbon in the substrate, was approximately the same for all samples.

Experiments with a mixed culture of microorganisms taken from cow's rumen fluid and from an anaerobic sewage plant digestor measured methane production. Again, pure glucose substrate was compared with acid hydrolyzate samples; results gave only low conversions to methane, which was thought to be due to additional organisms in the mixed culture, besides the methanogenic and acetogenic ones, which were converting the glucose to products other than methane.

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APPENDIX G

RECYCLING OF CELLULOSE

Exploratory studies have been carried out on recycling the unreacted cellulose present in the hydrolysis product to obtain additional glucose. The unreacted cellulose was recovered from the reaction slurry by filtration and then rehydrolyzed under the same reaction conditions as the ones used initially. Table G-1 shows typical initial experimental results. The additional amount of glucose obtained descreases sharply in terms of the total glucose yield with the second recycle. An alternative procedure would comprise mixing of the unreacted cellulose with fresh used newspaper feedstock in various proportions. Preliminary estimates of the cost effectiveness of such recycling techniques question the economic viability of such recycling. A more detailed economic study of the cost benefits of recycling is recommended.

TABLE G-1. EFFECT OF RECYCLING ON GLUCOSE YIELD FOR DILUTE SULFURIC ACID HYDROLYSIS AT 450 F

RUN	% GLUCOSE YIELD
450 F Acid Hydrolysis	51
With one recycle	59
With two recycles	63

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APPENDIX H

ORGANIC ACID CATALYSTS

The use of various organic acids in place of the usual sulfuric acid used for the dilute acid hydrolysis of waste cellulose has been experimentally investigated. Preliminary data for the glucose yields obtained with different organic acids are shown in Figure H-1. Maleic acid was found to be surprisingly effective in enhancing glucose yield, in fact comparable to sulfuric. Other organic acids, namely malonic, oxalic, and glutaric, were found to be significantly less effective than sulfuric acid.

Table H-1 shows that maleic acid catalyzed hydrolysis works best with hydropulped and irradiated newspapers. Use of this acid, which is of course substantially more expensive than sulfuric acid (some $3000 per ton vs $60 per ton, East Coast prices, September 1982), could ameliorate equipment corrosion problems and possibly also the rate of high temperature degradation of the glucose product.

TABLE H-1. MALEIC ACID CATALYZED HYDROLYSIS OF WASTE CELLULOSE (FEEDSTOCK: GARDEN STATE PAPER CO., USED NEWSPAPERS)

FEEDSTOCK PRETREATMENT	PERCENT SOLIDS	VOLUME ACID* (CC)	TIME (S[illegible])	TEMPERATURE (F)	% GLUCOSE YIELD
Hydropulping	5.1	80	60	450	32.5
Hydropulping & Irradiation	5.2	80	60	450	60.9
Hydropulping	5.0	160	40	450	30.0
Hydropulping & Irradiation	4.8	160	40	450	58.6
Hydropulping	11.0	150	40	420	16.5
Hydropulping & Irradiation	10.1	150	40	420	24.5
Hydropulping	5.0	80	60	450	32.5
Hydropulping & Irradiation	4.7	80	60	450	58.7

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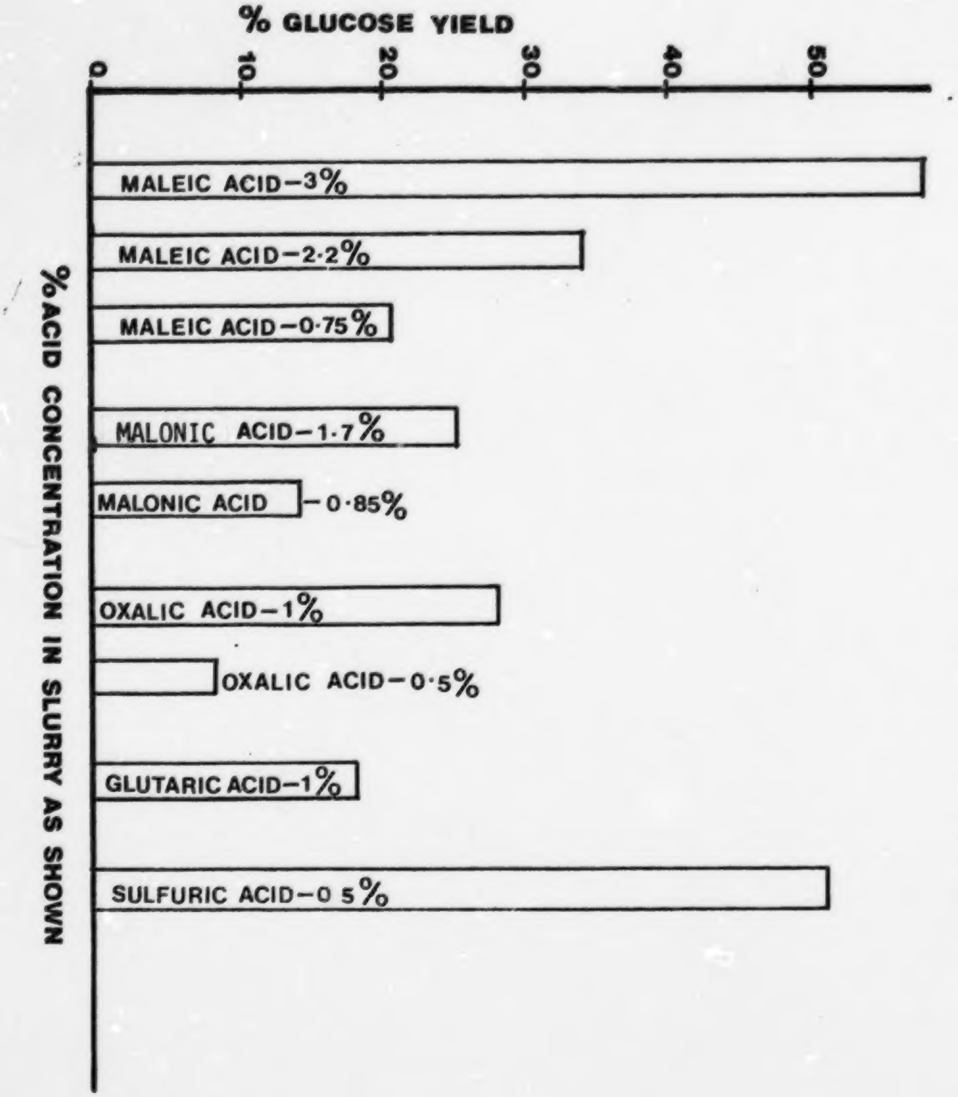

FIGURE H-1: Hydrolysis with Organic Acids (Wastepaper at 450 F, hydropulped and irradiated - 10 MR)